

THE MECHANISM OF THE BROMOWATERS OXIDATION OF 1-DECENE
IN EtCl_2 AND $\text{Et}(\text{ICl})/\text{Cu}(\text{Cl})$

By

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Abstract of Dissertation Presented to the Graduate School
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THE MECHANISM OF THE HOMOGENEOUS OXIDATION OF 1-BUTENE
BY BaCl_2 AND $\text{Ba}(\text{Cl})_2/\text{Cu}(\text{I})$

By

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The homogeneous oxidation of 1-butene by $\text{Ba}(\text{Cl})_2/\text{Cu}(\text{I})$ and by BaCl_2 was studied. This reaction was reported to be highly selective (80%) to forming the 1-butene (Hansen, E.; Bachmuth, R. M. F., *Trans Am Chem Soc*, **1958**, 80, 1078, 1082, 1087). The general mechanism proposed for these oxidations is the consecutive coordination of olefin and O_2 to a rhodium(I) complex, rearrangement to a peroxo intermediate, and decomposition to 2-butene product. The regeneration of the $\text{Ba}(\text{I})$ catalyst reportedly occurs in a second step involving Vacker-type oxidation of olefin. A subsequent study of this reaction reported that the catalyst is not a rhodium(I) complex, but is rather a rhodium(III) chloride complex (Elyberg, E. B.; Fritsch, R. C.; Bunch, R. B. *J. Am. Chem. Soc.*, 1962, 84, 3380). It was also reported

that in the absence of copper, only one oxygen atom was used in each 2-hexanoic. Further, it was reported that peroxide may be used as the oxidant in these reactions.

In this study, it was found that in the absence of copper, aldehydes or ketones form various oxidation and $\beta_{\alpha}\beta$ are formed continuously with 2-hexanoic. Coupling alcohol oxidation and aldole dehydratation reactions also occur in the absence of copper. The oxidation with peroxide is very similar to the oxidation with O_2 . Copper(III) facilitates a Wacker-type oxygen transfer in the absence of O_2 or peroxide. Mechanisms have been proposed for both the Hg^{2+}/O_2 and Hg^{2+}/H_2O_2 systems. The Hg^{2+}/O_2 mechanism proceeds via a two step oxidation in which the first step is the formation and decomposition of a peroxomercetoligand and the second step is a Wacker-type oxidation. Unlike the mechanism proposed by Rimeau and co-workers, the peroxomercetoligand is formed from the reaction of Hg^{2+} with O_2 . The Hg^{2+}/H_2O_2 is formed from the reaction of $Hg(III)$ with H_2O_2 . The H_2O_2 is formed by reduction of H_2 with $Gd(III)$. In the absence of copper, H_2O_2 is produced via a cycle in which alcohol acetone is continuously oxidized.

CHAPTER 1 GENERAL INTRODUCTION

The oxidation of organic compounds has been studied extensively in the last 40 years.¹ Whereas early studies of hydrocarbon oxidations focused on the identification of these processes, the availability of lower alcohols formed as by-products in gasoline manufacturing and the demand for the various oxygenated products have led to great interest in promoting selective hydrocarbon oxidations. Although oxidation of organic compounds is usually thermodynamically favorable, kinetically it is often sluggish. Furthermore, once initiated, hydrocarbon oxidations can be difficult to halt short of carbon dioxide and water. Selective partial oxidations can be achieved through the use of metal catalysts.

The success of the Wacker process for acetaldehyde production has led to the increased use of homogeneous catalysts in the petrochemical industry.^{2,3} Homogeneous catalysts are generally more active and selective than heterogeneous catalysts. This means that less severe reaction conditions can be employed and that fewer products are obtained in a particular reaction. For the researcher,

Heterogeneous catalysts also have the advantage that they are often more easily characterized than their homogeneous counterparts.

Many catalyzed reactions have been classified as either homogeneous or heterogeneous.¹ Homolytic processes involve one-electron changes in the metal species involved, usually first row transition metal salts (homogeneous) or metal oxides (heterogeneous). Organic free radicals are generated as intermediates in these systems. Very often the only role of the metal complex is to initiate free radical autoxidation by decomposing trace quantities of peroxides. These reactions generally exhibit poor product specificity, although in certain cases one product may predominate.

Heterolytic processes involve two-electron changes in the metal catalyst, and organic free radicals are not produced. These latter reactions are more specific because the principal bond breaking and reforming steps occur at the metal catalyst center. Among the most common reagents used in heterolytic catalysis are acids, peroxides, and aldehydes. Oxygen is the most attractive of these, owing both to its abundance and its favorable energetics.

The Wacker-Gelbo process²⁻³ for the production of acetaldehyde from ethylene employs a PdCl₂/CuCl₂ catalyst. Although O₂ is the terminal oxidant in this system, water reacts directly with a palladium-olefin complex to form products. The resulting PdO is reoxidized by CuCl₂.

producing CuCl , which may itself be reoxidized by molecular oxygen. The following reaction sequence has been proposed:¹



The mechanism for this reaction has been studied extensively,^{1,2-10} a mechanism consistent with experimental data involves sigma-allyl coordination to palladium(II), a π -to sigma rearrangement of coordinated allyls with cross coordination-ary through concerted attack of water, and a hydrolytic elimination of the hydroxyethyl-palladium(II) intermediate. The role of the copper(II) co-catalyst may extend further than a simple re-oxid function. For example, copper(II) chloride has been shown to cleave palladium-carbon bonds. Without copper(II), the reaction is self-stoichiometric, and metallic palladium is formed. Recently, the copper(II) reagent has been replaced by phosphamolybdate ions.¹¹

The $\text{Pd(II)}/\text{Cu(II)}$ system will also exhibit progressions and deviations in behavior in good yields.^{1-3,8} However, higher catalyst gives varying yields due to steric considerations. This system also displays selective nucleophilic substitutions with nitrates, alcohols, and amines by a similar intramolecular process to that described above, as intramolecular nitrates, producing α -nitroalkyl products, is possible for other nucleophiles such as vinyl, allyl, and

hydride.¹⁰ Other group VIII metal salts with similar effect on catalytic rate have been effectively.⁴

The various rhodium chiral complexes $[\text{RhCl}_2(\text{C}_2\text{H}_5)_2]^{1+}$ and $[\text{RhCl}_2(\text{C}_2\text{H}_5)_2]^{2+}$ have been used as catalysts for the oxidation of ethylene to acetaldehyde in aqueous solution.¹²⁻¹⁴ As oxidant, iron(III), copper(II), chromium(VI) or cerium(IV) is stoichiometrically consumed to regenerate the rhodium(III) catalyst by oxidation of rhodium(I) formed in the reaction. The mechanism proposed for ethylene oxidation by Rh(III)/Fe(III) is similar to that for the Pd(II)/Cu(II) system. In this case, however, it was concluded that a ligand water molecule was necessary for the activation process. Ethylene coordination to the Rh(III) is the rate determining step, migration of a hydride ligand results in formation of the edge bonded Rh(III) π -acetylaldehyde intermediate and β -hydride elimination yields acetaldehyde and Rh(I) . Palladium chloride was found to be twice as active as catalyzing this reaction as rhodium chloride under the same conditions.

The most known examples of heterolytic catalysis using peroxides as oxidants are the group VI and VII metal catalyzed epoxidations of alkenes.^{1,15-22} Propylene oxide is produced from propylene and tert-butylhydroperoxide in this way commercially. The active catalyst in these reactions is an inorganic peroxide, generated by binding hydrogen peroxide or alkyl hydroperoxide to an oxometal group. The metal is generally in its highest oxidation state. The substitution

of mineral for hydrogen tends to make the peroxide oxygen more electrophilic. This has been confirmed by substitution effects on the initial enolizes. The high yields and stereospecificity of products obtained in these reactions indicate a heterolytic process is occurring. However, a competing acid catalyzed homolytic decomposition of hydroperoxides may also take on by-products.

There are two types of mechanisms generally proposed for epoxidations employing alkyl hydroperoxides.^{1,24,25} In the first type, the hydroperoxide is converted to a peroxo-metal intermediate, which then reacts with olefin. In the second type, the alkyl hydroperoxide itself, bound to the metal center, is directly involved in oxygen transfer through an intramolecular nucleophilic attack. Generally, Krasov has proposed an intramolecular attack as a more direct olefin by alkylperoxo ligand through a peroxometal-olefin intermediate.^{1,24-26} Mechanisms for hydrogen peroxide as the oxidant are described similarly. Other nucleophilic reagents, such as oxides and sulfides, may undergo oxidation in this way.

Recently, transition(V) vanadium complexes of the type $\text{VO}(\text{O}_2)(\text{Phe})\text{L}_2$ and $[\text{VO}(\text{O}_2)(\text{Phe})_2]^{2+}$ (where Phe = pyridine-2-carboxylate, $\text{L}^+ = \text{R}^+$, PPh_3^+ and $\text{L} = \text{R}_2\text{O}$, EDT) have been reported²⁷ which can both epoxidize olefins and hydrolyze hydrocarbons, unlike the Mn analogues. The proposed mechanism involves $\text{V}(\text{IV})-\text{O}-\text{O}^-$ as the active species.

in organic solvent, hexafluoroantimonate,^{30,31} has also been used to oxidize olefins with H_2O_2 , furnishing regular to regular products. Antimony polypyrrole resin may also be used to catalyze olefin oxidation in bi- and tri-phase systems with H_2O_2 .³²

Whereas oxidation of olefins with ethylhydroperoxide yields regular is the presence of electrophilic peroxo metal complexes, the same reaction with nucleophilic peroxo metal complexes of the group VIII metals yields regular isomers. Shono and co-workers³³ have employed a tetrameric rhodium-peroxodichloride(III) species which inserts a terminal olefin to give a 4-peroxyalkyl alkyl. A 4-hydroxy migration produces the methyl ketone product. Similarly, a dimeric ethylperoxyplatinum(II) species has been reported³⁴ which also oxidizes terminal olefins. In the presence of excess 1-butanol, these systems can both isomerize, producing regular turnover in the case of the platinum complex. Another catalytic system employs palladium(II) acetate and H_2O_2 to oxidize 1-octene to 2-octanone in acetic acid or 1-butanol solvent.³⁵ Also formed in this reaction were 3- and 4-octanone. A palladium catalyzed decomposition of H_2O_2 also occurred.

These systems are strongly affected by variations in the surrounding ligands. Influence of the nucleophilic acetate group by the electrophilic trifluoroacetate group strongly accelerates the olefin oxidation.³⁴ Presumably,

abstracting electrons from the porphyrin oxygen when there were susceptible to nucleophilic attack by the olefin.

The mechanism which has been proposed in these reactions is very similar to one which has been described for the polydimethylsiloxane olefin epoxidation reaction. The allylsiloxanemetal complex coordinates olefin, and in an intramolecular reaction, the nucleophilic *tert*-butylperoxide group attacks the electrophilic coordinated olefin, forming a quasi-peroxy-metalloperoxide intermediate. Decomposition of this adduct with β -hydride migration produces methyl ketone and a metal *tert*-butoxy complex.

A monomeric *tert*-butylperoxy complex of platinum(II) was also shown to oxidize linear terminal olefins to methyl ketones,³⁰ but only when the arrangement of the phosphine ligands on the platinum was trans. Besides the two phosphine ligands, an alkyl ligand bearing electronegative substituents was used to stabilize the peroxo complex. More recently, $P_2Pt(CH_3)_2(OR)_2$ complexes (P_2 = *trans*-diphosphine, OR = activated alkyl or aryl) have been reported³¹ to be active catalysts for the epoxidation of olefins with H_2O_2 .

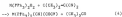
The search for catalysts which could utilize molecular oxygen in a catalytic process began in the 1960's with the discovery that Paine's complex reversibly binds dioxygen.^{1,32} It was subsequently found that monomeric peroxo complexes of group VIII metals are indeed capable of oxidizing a variety of substrates in both stoichiometric and catalytic reactions.^{1,33-41} The most widely studied

complex, $(\text{Ph}_3\text{P})_2\text{PtO}_2$, was found to oxidize SO_2 , H_2 , H_2S , CO , CO_2 , CS_2 , phosphines, aldehydes, ketones, and nitriles.³⁹⁻⁴⁷ Some of these reactions are catalytic. For the most part, these reactions have been proposed to proceed by a mechanism which involves an intramolecular reaction between coordinated diogenes and substrate.

Both platinum and palladium complexes of the form $\text{M}(\text{Ph}_3\text{P})_2\text{O}_2$ were found to react with electrophilic alkenes,⁴¹ alkenes substituted with electron-withdrawing groups, such as

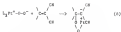


These electrophilic alkenes proceed according



Since heterogeneous is the form of dimersubstituted group-metallocenes were involved and characterized. The palladium catalyst is unstable and decomposes at room temperature. Kinetic studies have shown that two reaction pathways are proceeding simultaneously. The major pathway involves pre-coordination to a vacant axial site on the metal, followed by insertion. A minor pathway, however, which is anti-order

is substrate, suggests polar coordination of diorganotin with coordination to an end-on bonded form, followed by nucleophilic attack on the coordinated center.



There is evidence that this latter type of mechanism is operating in the $(\text{Ph}_3\text{P})_2\text{PtO}_2$ catalyzed oxidation of phenol.¹² In this case, it was shown that $(\text{Ph}_3\text{P})_2\text{PtO}_2$ reacts with a molecule of Ph_3P to form a 1,3-diphenylacetone.



in ethanol or other protic solvents, molecular hydrogen from hydrazine, which acts as the oxidant.



Simple alkenes, however, do not react with $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ or the palladium analogues.

Recently, it was reported⁴⁹ that addition of stoichiometric excess of the strong acid HClO_4 to an anhydrous solution of $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ in CH_2Cl_2 /1-octane resulted in the production of 1-octanol (50%) and Pt_2Cl_2 (54%). But $\text{HClO}_4 \cdot \text{H}_2\text{O}$ was less effective in promoting this reaction. Strong alkylating agents such as $\text{Ph}_3\text{C}^+\text{BF}_4^-$ or MeSO_3^+P also effected 1-octanol production, though in smaller yields. Presumably, strong acid or alkylating agent would generate Pt-OH or Pt-OOR from palladium-dioxygen adducts. Facile oxidation could then occur as previously described. No 1-octanone is formed with the platinum analogues $(\text{Ph}_3\text{P})_2\text{PtO}_2$.

There have also been examples of stoichiometric⁵⁰ and catalytic⁵¹⁻⁵³ heterocyclic oxygen atom transfer reactions via coordinated alkenyl groups. Catalytic oxidations of simple alkenes and secondary alcohols have been reported using metal-oxo complexes of palladium and cobalt.^{55,56} Also, $\text{Pt}(\text{CH}_3\text{CN})_2\text{Cl}(\text{H}_2\text{O})$ oxidizes terminal alkenes to methyl ketones. The catalyst is regenerated by exposure to O_2 . Thus, dioxygen is the terminal oxidant in this system. In

oxygen behaving as a π -acid⁵¹ has established that the ether group is in fact the copper source. The proposal that a acetaldehyde is an intermediate in this reaction is supported by EPR evidence.



Alkenes may be oxidized in metal-catalyzed reactions.^{51,52} Epoxidation occurs when π -hydride alkenes is not feasible (e.g., when alkenes are sterically blocked from achieving the σ^2 H-C-C-C dihydropyridine geometry for π -hydride alkenes).

The first real example of a selective, non-radical oxidation of simple alkenes by O_2 was the stoichiometric oxidation of terminal alkenes in the presence of $RhCl(PPh_3)_3$ or $Rh(PPh_3)_3Cl_2$.^{54,57} This reaction, run in benzene solvent, produced a 7/1 mole ratio of β -ketone and cleavage aldehydes. In the absence of olefin substrates, approximately two moles of O_2 were taken up per Rh complex, and two moles of Ph_3PH were produced. Because $RhCl(PPh_3)_3$ is known to decompose hydroperoxides, one can take its role as a free radical oxidant. However, ketones and aldehydes are not the normally observed products in such reactions. Addition

of the radical inhibitors hydroquinone and 2,6-di-*t*-butyl-4-methylphenol did not affect the product yields.

In the presence of excess PPb_2 , the 1-hexene oxidation became catalytic,⁵⁸ producing four turnovers in an hour. Phosphine was proposed to reduce the oxidized rhodium latero-oxides to rhodium(I), thus regenerating the catalyst.



In this system, seven times more phosphine oxide was produced than 1-hexene. A second, competing Rh-catalyzed phosphine oxidation was proposed to occur,



The possibility that a Wacker-type sp^2 -metathesis was occurring seemed unlikely, since added water was found to inhibit the reaction slightly. Further studies adding ^{18}O labeled water to the system showed no label incorporation into either ketone or phosphine oxide product.⁵⁹

The mechanism proposed for this system is illustrated in Figure 1. Decaying phosphine was suggested to partly dissociate the peroxo ligand to the 1,3-digonal face. Intramolecular nucleophilic attack of the peroxo ligand on coordinated alkene produces a five-membered peroxametallacyclic cycle, analogous to those seen in the reactions of $\text{FeCl}_2(\text{PPb}_2)_2$ with nucleophiles. Subsequent elimination of a diene from the peroxametallacyclic intermediate and the

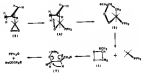


Figure 2. The mechanism proposed by Reed and Walker¹¹ for the inhibition of cationic isoprene with S_2 in the presence of $\text{EtMg}_2(\text{PPH}_3)_2$.

subsequent decomposition was proposed to account for product formation. An alternative decomposition of the peroxyphosphinic complex could, however, produce ketone and an azido-diazo(III) species. The phosphine sulfonate reacts with azobisisobutyronitrile(III) could also regenerate the RhCl_2 catalyst.

Similar RhCl_2 catalyzed oxidation of styrene to acetophenone and benzaldehyde were also reported.²⁰⁻²² Several complexes of other group VIII metals were investigated as catalysts, including complexes of Ir, Pd, Pt, and Ru, but none were effective as catalysts. Also, $\text{RhCl}_2\text{PPh}_3$ was not effective as a catalyst for this reaction. Significantly, no correlation was necessary for catalyst activity. Although the acetophenone product was not affected by the addition of 2,2-di-*t*-butyl-4-azobiphenol radical inhibitor, benzaldehyde production decreased considerably. Further, in the presence of the radical inhibitor 1-hydroperbenzoate, acetophenone production is unaffected, but benzaldehyde production increases drastically. These results indicate that while acetophenone production arises from a homogeneous process, benzaldehyde production results, at least in part, from free radical autooxidation. Data was also taken to rule out a Wacker-type oxidation. Addition of varying amounts of water had no effect on the reaction rate. Also as ^{18}O label in H_2O was not incorporated into the acetophenone product. The rate law found for acetophenone production suggests that

$$\text{rate} = \frac{K[\text{styrene}][\text{catalyst}][\text{O}_2]}{1 + K'[\text{H}_2\text{O}]} \quad (14)$$

coordination of oxygen and nitrogen to Rh(I) may occur prior to the rate determining step. Ferrer and co-workers note⁴⁵ that under an atmosphere of oxygen, the oxidation is insensitive to oxygen concentration.

A third Rh(I) catalyzed oxidation reported^{44,45} oxidized cyclohexene to cyclohexanone and cyclohex-3-ene-3-one with $[\text{Rh}(\text{C}_6\text{H}_{14})_2\text{Cl}]_2$. Water is also produced in the reaction. Experiments using free radical inhibitors and inhibitors showed a free radical chain autoxidation mechanism to be ruled out. Two studies mapping the Rh^0 concentration and addition of ^{103}Rh labeled Rh_2O_3 were used to rule out a Fenton oxidation. However, the $(\text{Ph}_2\text{P})_2\text{RhCl}$ catalyzed oxidation of cyclohexene was shown to proceed via a Fenton-Wiles decomposition of cyclohexene hydroperoxide.⁴⁶⁻⁴⁸

These examples of heterocyclic olefin oxidations by O_2 exhibit neither the activity (turnover ratio from 5 to 35 in 24 hours) nor the selectivity (since more than one product is formed in each case) that was anticipated for a metal catalyzed oxygen transfer reaction. However, the reaction reported by Merson and co-workers^{49,50} uses a 1:2 rhodium(III)/copper(II) catalyzed system to oxidize hex-3-enal alcohol to 3-ketone with 98% selectivity with respect to atmosphere of oxygen used:



Best selectivity about this system is the high specificity for 3-ketone product, the utilization of both oxygen atoms

of diorganotin to form this product, and the dependence of the initial rate law on diorganotin pressure.

The reaction proceeds at 40°C, producing more than 180 barbitone in 4 hours. It is most active in ethanol or isopropyl alcohols. In other alcohols, such as 1-methoxy-ethanol, acetone, 2-butanol, and n-hexanol, the activity is decreased somewhat. The catalyst is less active in acetone and methylcetyl ketone, and inactive in chlorinated solvents, nitrobenzene, DMF, acrylonitrile, and THF. The reaction may also be run in benzene, toluene, or ethyl acetate in the presence of small amounts of ethanol.

This system is most active when three equivalents of chloride per rhodium are present. It was reported that large increases in the catalytic activity (two orders of magnitude) are obtained when the Cl/Rh ratio is increased from one to three, employing either $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ or $[\text{Rh}(\text{C}_6\text{H}_{14})_3\text{Cl}]_3$ as the catalyst precursor. However, a five to one chloride to rhodium ratio (rhodium(III) chloride plus copper(II) chloride) is sufficient as a catalyst at 40°C.

Incidentally, a $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ catalyst precursor is more active than is $[\text{RhCl}(\text{C}_6\text{H}_{14})_3]_3$. Either Co(III) or Fe(III) may function as the co-catalyst. In the absence of a Co(III) or Fe(III) co-catalyst, both the activity and the oxygen specificity are greatly reduced. Substitution of Ag^+ , Li^+ , or Mg^{2+} gave inferior results.

When Cu(II) is used as the co-catalyst, a precipitate of CuCl is observed, which may be isolated in 70% yield and removed from the mixture without adversely affecting the reaction. Thus, one function of the copper co-catalyst is the production of anionic species. The co-catalyst may also enhance the reaction by virtue of the redox properties, and may serve as a terminal R_2 species. However, in the absence of R_2O , Cl^- , and Cu(II) , Sn(III)_2 catalyzes olefin oxidation, producing the same 1-hydroxy products. For this reason, no direct role for the copper co-catalyst in the oxidation was proposed.

Great care was taken to show that R_2O is not involved here as the direct oxidant as in the Markov process. In fact, R_2O inhibits the reaction. Neither aldehydes nor internal ketones are produced, as in the palladium system. In that system, aldehydes result from the anti-Markovnikov addition of OH^- to olefins coordinated to the palladium center. Internal ketones arise from the oxidation of internal olefins, formed by isomerization. In contrast, in the Sn/Cu system, only terminal olefins, not linear internal olefins, are oxidized and very little olefin isomerization is observed. With cyclic internal olefins, the activity and products obtained vary with the substrate. In the case of cyclopentene, the major product is the allylic ether, resulting from the allylic substitution of olefin at the α position of the double bond. Thus, the products may be traced to the nature of the olefinic bond. Finally, ¹⁸²

labeling studies have shown that the oxygen in ketone product comes from O_2 exclusively.²¹

Unlike the previously reported $RhCl$ catalyzed oxidations with O_2 , the observed rate law for this reaction is independent of oxygen pressure from 400 to 1100 torr O_2 .

$$\text{rate} = k_p[\text{rhodium}][\text{olefin}][O_2]^0 \quad (10)$$

Although $RhCl_3$ is most effectively employed as the catalyst precursor, $RhCl$ is thought to be the active catalyst. The $Rh(I)$ catalyst may be produced by the ethanol solvent reduction of $Rh(III)$. The stoichiometric formation of oxetane-type was observed in the early stages of reaction and was taken as evidence for this reduction.

The proposed mechanism, illustrated in Figure 2, is composed of two complementary reactions. It includes the classical carbene reduction of $RhOH_3$ and $Co(III)$ to $Rh(I)$ and $Co(I)$ in an initiation step, followed by the coordination of both olefin and O_2 to $Rh(I)$, insertion of olefin into the $metal-O_2$ bond, and rearrangement to a five-membered peroxy-metalacycle. This cyclic intermediate decomposes via β -hydride migration to 2-butenes and a rhodium-oxo complex. The oxo complex is hydrolyzed by acid to a rhodium hydroxide complex. The rhodium(II) catalyst is proposed to be regenerated by oxidation of a second olefin to 2-butenes in a Wacker-type process involving a rhodium-oxetane species.

Support for the slow part of this mechanism comes from the reaction of oxidized olefins with rhodium dihalides

complexes of general formula $[\text{RuO}_2\text{L}_2]^{2+} \text{ }^{1-}$, producing methyl ketones.⁷¹ Similarly, the reaction of Os_2 with various rhodium(III)-cyclic complexes such as $[\text{Rh}(\text{L}, 7\text{-} \text{acetylenyl})_2]^{2+} \text{ }^{1-}$ in alcohol solvent produces 3-acetyl-2-one and water.⁷² In the presence of a strong acid, only the ketone was produced. Further, a peroxorhodium(III) intermediate was isolated from the reaction of the rhodium deoxy- gas complex $[\text{RhO}_2(\text{NaO}_2)_2]^{2+} \text{ }^{1-}$ with the electrophilic cyclic tetraacyanethylene (TCE). A similar intermediate has been isolated for palladium and has been proposed for the copper(II)-catalyzed oxidation of alcohols.

This mechanism is very similar to one which has been proposed for the oxidation of terminal alcohols to methyl ketones with allylpyridineoxide using a terminal peroxide(II) complex.⁷³ The similarity between these two systems was explicitly mentioned by Hinson and coworkers in the report on the palladium catalyst.

Szyba⁷⁴ studied the rhodium-catalyzed reaction in both the presence and absence of the copper(II) complex. He reported that only one product of Os_2 was used in some ketone product in the absence of copper(II). Since the complete oxidation of Os_2 requires 4 electrons, and 2-hexanol is provided only two, a third solvent was proposed to reduce the second 2-hexol to produce H_2O and regenerate the catalyst.

Szyba and co-workers^{72,75} implicated rhodium(III) chloride as the catalyst in the $\text{Os}(\text{III})/\text{Ru}(\text{III})$ -catalyzed cyclic oxidation. They reported the oxidation of

$[\text{Rh}(\text{NO})_2\text{Cl}]_2$ or RhCl_3 and the correlation between the production of the rhodium(III) chloride complex and the initiation of the catalytic oxidation of olefins. Furthermore, it was determined that isopropanol solvent provides only enough reducing equivalents to stoichiometrically convert Rh(III) to Rh(I) (isolated as RhCl in 80% yield¹⁸), eliminating the extensive reduction of RhCl_3 to Rh(I) . Compelling evidence for the existence of rhodium(III) in the catalytic mixture is the dependence of initial olefin oxidation rates on chloride ion, as mentioned previously. The marked olefinic influence on catalytic activity cannot be accommodated by a proposed mechanism nearly complete conversion of rhodium(III) to a rhodium(I) catalyst.

This characterization of the active catalyst as a Rh(III) chloride complex is important, since Rh(III) is not expected to coordinate olefins. Either the Rh(III) or the O_2 must be reduced prior to reaction. Epling reported that H_2O_2 could be used effectively as the oxidant in the rhodium-catalyzed olefin oxidation both with and without the copper co-catalyst. Further, this reaction could be carried out in *t*-butanol solvent, eliminating the possibility that solvent reducing equivalents play a role in this reaction. The use of *n*-BuOH produced faster oxidation rates than did H_2O . With peroxide as oxidant, Epling reported that even in the presence of the copper co-catalyst, a mixture of *anti* 2-ol was interpreted with 2-ketone product.

Because of the similarity in the products and catalysis between the H_2 and HDO oxidations, Sykes proposed that possible is the direct oxidant in the H₂-catalyzed reaction. He limited a role for Cu(I) to reducing H_2 to cuprous peroxide which reacts with HCl_2^+ to form the active complex $[\text{CuCl}_2(\text{OOH})(\text{CH}_3\text{-CHO})]$ (as opposed to Koser's $[\text{Cu}(\text{CH}_3\text{-OOH})_2\text{O}_2]^{2+}$). This species could be produced in the absence of copper by alcohol oxidation of H_2 . The reduction of O_2 by Cu(I) avoids the need for this alcohol oxidation. No direct evidence was given for this proposed role of copper. The steps after formation of the active complex were proposed to be similar to Koser's. The proposal that CuCl reduces H_2 is reminiscent of the role of copper in the Wacker cycle, in which Cu(II) reduces H_2 to H_2O , which then coordinates to Pd(II).

Since the report of the H₂/Cu catalyzed oxidation of aldehydes, a second example of a system which oxidizes hydrocarbons with molecular oxygen, using both oxygen atoms to form product, has been reported.²⁴ Bisoxetetrakis(porphyrinato)cobaltocenyl(TE) $[\text{Co}(\text{TPP})(\text{B})_2]$ catalyzes the oxidation of aldehydes at ambient temperatures and pressures, without a co-catalyst. Two series of species are postulated for each mode of O_2 cleavage.

This system is the result of efforts to avoid the toxicological conditions of asymmetric P-450. Since various intermediates have been implicated in the P-450 mechanism,^{1,24} most model systems employ cobaltocenes.

complexes, such as tetraphenones or hypochlorite ion. With $\text{Ru}(\text{DTP})(\text{OH})_2$, oxidation proceeds with retention of configuration, similar to other metalloporphyrin oxidations with tetraphenones. Also similar to other metalloporphyrin systems, the rate of oxidation is much more sensitive (15 times) than the true barrier.

Like Simon's $(\text{Ru}_2\text{P}_4)_4^{2+}$, $\text{Ru}(\text{DTP})(\text{OH})_2$ will oxidize olefins stereoselectively under suitable conditions. The oxidation of $\text{Ru}^{\text{II}}(\text{DTP})(\text{DTP})_2$ in air yields $\text{Ru}^{\text{IV}}(\text{DTP})(\text{OH})_2$. Tetra-*n*-butylporphyrin, which forms μ -oxo dimers, produces no oxidative catalysis.

The proposed mechanism involves $\text{Ru}(\text{DTP})(\text{O})_2$ reacting with olefin to yield epoxide and oxoruthenium(IV) complex, which may disproportionate to the dimeroxoruthenium(IV) complex and $\text{Ru}^{\text{II}}(\text{DTP})$. This latter species reacts with O_2 to reform oxoruthenium(IV). In support of this mechanism, the UV-visible spectra of active solutions show an $\text{Ru}(\text{IV})$ and little $\text{Ru}(\text{II})$.

CHAPTER 2
THE REDUCTION OF THE HOMOCYCLIC OXIDATION OF 1-BUTENE
BY SnCl_2

Background

The homogeneous oxidation of 1-butene by SnCl_2 was studied because of the similarities to the Rh/Cu -catalyzed system, as pointed out by Hinson and co-workers,⁴³ and because of the differences between the two systems, as pointed out by Ryland and co-workers.^{22,72}

Hinson and co-workers⁴³ noted that in the absence of a copper co-catalyst, the same 1-butene product was produced. With the rhodium(I) precursor $(\text{RhCl}(\text{C}_6\text{H}_5)_3)_2$, 1-butene was oxidized stoichiometrically to a mixture of 1-butanol (82%) and butanal (18%). With the addition of KClO_4 or SnCl_4 , the system is catalytic, producing 8 butenols in 4 hours. When $\text{Rh}(\text{Cl}(\text{C}_6\text{H}_5)_3)_2$ is used as the catalyst, 17 butenols are obtained in 4 hours. 2-Pentanol (4%) is also produced. Thus unlike the presence of copper or chloride ion is necessary for catalytic activity, although the Rh/Cu system is about 5 times more active. The specificity with respect to the oxygen consumption is poor compared to the Rh/Cu system. Because of these similarities, Hinson and co-workers assumed

that similar reaction mechanisms were operative. In fact, no specific rule for copper in the Hg/Cu -catalyzed reaction schemes was proposed.

It is interesting that rhodium(III) procedures are more active and specific for 2-butenes product than rhodium(I) procedures. The cleavage alkylide product was proposed to result from an alternative decomposition of the five-membered metacyclopentadiene intermediate (described in Chapter 1), involving the rupture of the C-C bond. Oxidative cleavage has also been reported to occur with $\text{RhCl}(\text{PPh}_3)_3$ by bond and coworkers^{87,88} in the oxidation of 2-butenes to polarisily 2-butenes, and by Balland and Silber⁸⁵ in the oxidation of styrene to acetylbenezene and benzaldehyde. In the latter case, benzaldehyde production was shown to result, at least in part, from free radical autoxidation. Merson and co-workers suggested⁸⁹ that the Rh(III) met intermediate (produced from the reaction of $[\text{Rh}(\text{CH}_3\text{-CH=CH})_2\text{Cl}]^+$ to give 2-butenes) may be capable of oxidative cleavage of olefins through a $[\pi + \pi]$ interaction. The four-membered intermediate could decompose to alkylide and a olefin metacyclopentadiene complex. This pathway was suggested to occur in the absence of acid or a phosphine reducing agent.

Merson and co-workers also suggested⁸⁹ that the products of olefin oxidation could be traced to the olefin interaction. Terminal olefins, which give methyl ketone products, produce an olefinic $\text{RhCl}(\text{P})_2$ -complex. Other

substitution, such as cyclopentadiene, glycerol-olipide complexes with rhodium(III), and some alipide ethers as products from the oxidative substitution of alcohol at the α position of the olefin. Oxidative substitution does not require activation of O_2 by Rh(II), and was proposed to occur via nucleophilic attack of a coordinated alkene ligand on a Rh(III)/ π -olipyl complex. Cyclopentadiene is also observed to take reaction and was proposed to result from a classic Heckler oxidation. With cyclopentadiene, R_2S does not have an inhibitory effect, in contrast to the case with terminal olefins.

Sykes and co-workers^{12,23} pointed out profound differences between the RhCl₃ and the Rh/Co-integrated olefin reactions. Based on the proposed need for Rh(II) to complex olefin and O_2 , [Rh(CO)₂Cl]₂ was used as the catalyst precursor. Similar to Sykes's experiments with a [Rh(Et₃Si)₂Cl]₂ precursor, two equivalents of acid were necessary for maximum catalytic activity. An induction period was observed with the [Rh(CO)₂Cl]₂ precursor. The length of the induction period was found to depend on the dioxygen pressure. The slow reaction of [Rh(CO)₂Cl]₂ to form active catalysts is not expected for the simple substitution of R_2 and 1-hexene for labile CO ligands and implies that a more complicated reaction than ligand substitution at Rh(II) is taking place.

Study of the induction period showed that [Rh(CO)₂Cl]₂ was oxidized to a rhodium(III) chloride complex (equation 17) before oxidation of 1-hexene occurred.



No induction period is observed when $\text{RhCl}_2(\text{OH})_2$ is used as the catalyst precursor. Munro and co-workers did not report⁴⁸ the presence of an induction period with $[\text{Rh}(\text{C}_6\text{H}_4)_2\text{Cl}]_2$, either with or without added acid. These results are consistent with Munro and co-workers' findings that $\text{Rh}(\text{III})$ produces a more active catalyst than does $\text{Rh}(\text{I})$.

This characterization of the catalyst as a rhodium(III) chloride complex is significant, since $\text{Rh}(\text{III})$ is not expected to coordinate dioxygen. The reduction of O_2 to HO_2H prior to interaction with the $\text{Rh}(\text{III})$ complex was considered by Ryberg.⁷¹ The interaction of HO_2H with $\text{Rh}(\text{III})$ is reasonable, and Ryberg points out that this reaction has been described in the literature.

Ryberg found⁷² that HO_2H and $\text{HO}_2\text{O}_2\text{H}$ are effective oxidants for olefin oxidation with RhCl_3 and $\text{Rh}(\text{III})/\text{Co}(\text{II})$ under inert atmosphere. This reaction also occurs in *in vacuo*, eliminating the possibility that solvent redox equivalents play a role in olefin oxidation with peroxide oxidants. Ryberg suggests that the mechanism may be similar to that proposed by Munro and co-workers for the oxidation of alkenes with peroxide employing a tetrameric palladium catalyst.

However, Ryberg observed⁷³ that the order of addition of reagents was critical. The peroxide oxidant must be

added before the 1-hexene, according to Syberg. This 1-hexene is added to the $\text{Ru}(\text{III})$ -containing solution before peroxide addition, as reaction scheme. The 1-hexene was proposed to saturate the $\text{Ru}(\text{III})$ complex, blocking coordination of H_2O_2 . It was not established why such a saturation does not occur in the presence of H_2 .

The effectiveness of peroxide as oxidant for both the RuCl_2 - and the Ru/Cu -catalyzed reactions supports the intermediary in the RuCl_2 - and Ru/Cu -catalyzed 1-hexene oxidations with O_2 . The similarities in the products obtained suggest that similar mechanisms are occurring with both oxidants. Peroxide may be formed in the reaction from primary and secondary alcohol reactions with O_2 , and $\text{Ru}(\text{III})$, $\text{Cu}(\text{II})$, and H^+ may catalyze this reaction.⁷¹ Alcohol reduction of O_2 was proposed to be a key feature of this reaction.

Syberg also showed⁷² that for the oxidation with O_2 in the absence of the copper co-catalyst, only one O-atom of O_2 was incorporated into 2-hexene product. This implies that H_2O is produced continuously with 2-hexene in this reaction (equation 10).



This is significant, because it implies that copper causes the second O-atom to be used to produce 2-hexene. At higher reaction temperatures, the alcohol reduction of O_2 to H_2O is

also occurring, accounting for the higher \bar{Q} -value consumption reported (3.8/1) (equation 19).



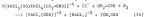
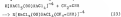
At higher temperatures, reaction 18 is more favorable relative to reaction 17.

Syberg⁷² found differences in the BaCl_2 -catalyzed reaction at 40°C and 70°C. At 70°C, 2-hexanol production was significant (38) compared to 2-hexanone. At this higher temperature, the rate law was found to follow equation 18.

$$\text{rate} = k[\text{Ba}]^2[\text{alcohol}] \quad (19)$$

The rate law for the BaCl_2 -catalyzed reaction at 40°C was not reported by either Syberg or Winans, but was assumed to be similar to the BaCl_2 -catalyzed reaction, which is third order in $[\text{Ba}]$ and $[\text{alcohol}]$ and first order in $[\text{O}_2]$ (equation 16). Syberg ruled out H_2O as the catalyst at 70°C.

Syberg proposed⁷² the following reaction sequence at 70°C to account for his observations—



benzene and methyl vinyl ketone were purchased from Aldrich and used as received.

Nitrogen peroxide (20%, Fisher) and isobutylphthalimide (20%, Aldrich) were standardized volumetrically.²⁶ Isobutylphthalimide was prepared as reported in the literature.¹⁷ The N-isobutyl-4-methylphthalimide (Matheson, Coleman, and Bell), 2,2',4,4'-tetrakis(isobutyl)-5,5'-bibenzophenone (Aldrich), pinacol boronate (Alfa), isobutene-2 (Aldrich), and tetrafluoroboric acid-diethyl ether complex (Aldrich) were used without further purification.

Apparatus

The 2-bromobenzoate production was measured by HPLC on a Varian model 940 with a flame ionization detector using a one meter, 1/8 inch I.D. copper column packed with Diethylene glycol adipate supported on Chromasorb P (column temperature 80°C), or on a Varian model 1900 with a flame ionization detector, using an eight foot, 1/8 inch stainless steel column packed with 30 Diethylene glycol adipate on Chromasorb P (column temperature 160°C). Cis- and trans-2-bromobenzoate were detected using an eight foot, 1/8 inch stainless steel column packed with Chromasorb 100 supported on Chromasorb P (column temperature 100°C). Water production was detected with a Chromat conductivity detector using an eight foot, 1/8 inch stainless steel column packed with Poropak Q (column temperature 170°C). Integration was performed by a Hewlett Packard model 1090A integrator, as previously

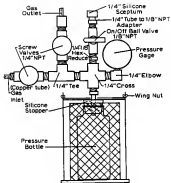
described.⁷³ GC-MS analyses were performed by Dr. M. Ting at the University of Florida.

Reactions were carried out in 228 ml Parr pressure bottles (Arthur H. Thomas Co.) equipped with brass or stainless steel hangfish pressure heads, and placed inside a steel mesh explosion shield (Figure 1). Samples were removed using a gas tight syringe connected to a syringe stopcock (Becton, Dickinson and Company) and a 12 inch, 18 gauge needle. An oil bath was used to heat the bottle openings.

This apparatus did not have any means to relieve pressure in the event of overpressurization (above the pressure rating for the Parr bottles). Overpressurization could be caused by gas regulator failure, failure of the temperature controller, or chemical reaction, for example. A relief device (such as a relief valve or rupture disk) should be added to the pressure heads for safety reasons.

The pressure was vented after a reaction through a safety valve. The gas released is saturated with volatile organic solvents. Explosive mixtures may be present, due to the use of pure oxygen gas. For safety reasons, all glass-lined apparatus to the head should be made explosion-proof. It is further recommended that before undertaking any modification, the design pressure of the vessel, possible causes for overpressurization, explosion limits, and the substitution of air for pure O_2 wherever possible be carefully considered.

Figure 3. Apparatus used for the oxidation of alkenes at pressures greater than 10 psig. The reaction mixture is placed in the pressure bottle, which is attached to the silicone stopper and secured using the wing nut. The bottle is filled with oxygen by introduction from the inlet. Pressure is monitored with the pressure gauge. Samples of the reaction mixture can be withdrawn without altering the pressure of the system by inserting a long needle attached to a gas-tight syringe into the silicone septum, through the open ball valve and into the pressure bottle. (Figure courtesy of D. E. Hadden^{1,2})



Synthesis Procedure

For a typical high pressure oxidation, 0.0018 g (3.4×10^{-5} moles) of the catalyst RhCl_3 , 45 mL solvent, 15 mL of substrate, and 0.30 mL (3.3×10^{-3} moles) of 2-octanone (KLC internal standard) were added to a 250 mL pressure bottle containing a magnetic stir bar. The bottle was attached to the pressure head and was then purged several times with O_2 before charging to the desired pressure. It was then placed in a constant temperature oil bath at 60°C and stirring was begun to initiate the oxidation.

The progress of the reaction was monitored by withdrawing 0.1 mL samples of the reaction mixture via the silicone septum. Products were analyzed by KLC. The amounts of products present were calculated from a calibration curve, using 2-octanone (or 2-heptanone) as the standard.

For oxidations with hydrogen peroxide, t-butylhydroperoxide, water, or no added oxidant, 0.0018 g of the catalyst RhCl_3 was weighed into a round bottom flask equipped with a magnetic stir bar and a rubber septum. The flask was then purged with nitrogen. Nitrogen-purged solvent (4.0 mL) was added and the solution was purged with nitrogen for 30 minutes. Nitrogen-purged 2-octanone (0.10 mL, known standard) and nitrogen-purged 1-hexene (1.50 mL) were then added to the flask. The flask was heated in a 60°C oil bath for five minutes. The desired amount of nitrogen-purged solvent

was then added by addition of the reagents. Samples were removed at intervals and products were analyzed by GLC.

Instrumentation

Electrochemical spectra were obtained from a Perkin Elmer 518 or a Cary 14 spectrophotometer. The UV spectra were obtained on a Varian 88-340-S spectrometer. Infrared spectra were run on a Perkin Elmer 521B infrared spectrophotometer. The NMR spectra were obtained on a Bruker 60 1000-580 spectrometer or a Varian Model A-6 spectrometer equipped with a Hewlett Packard frequency counter.

Results and Discussion

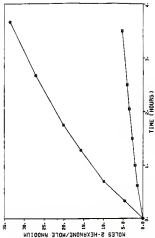
Activity

In Figure 1 is presented a comparison of the activity of the RuCl_3 and Ru(III)/Os(III) catalyst systems for 1-bromo oxidation. The reaction concentration employed in each case is 0.001M, only 12.5% that employed by Hinson and co-workers.^{6b} When RuCl_3 is used, only 3.5 turnovers (mole 1-bromo per mole RuCl_3) are observed in 1.0 hours, although the catalyst is still quite active at this point. In contrast, the Ru(III)/Os(III) co-catalyst (1:1 mole Os/mole Ru) produces 32.5 turnovers after 2.0 hours under identical conditions. These results are in good agreement with those reported by Hinson and co-workers^{6b} and Hyatt,¹² who report that the rate of oxidation (and the turnover

Figure 4.

Confidence of 3-lyons (100%) with ϕ_1 as relevant (100%).
 Transformation = 100%, pressure = 100%, ϕ_2 .
 Confidence 100%, (0.00000) significant.
 Confidence 100%, (0.00000) significant.
 Confidence 100%, (0.00000) significant.

(O) 100
 (●) 1000



specificity) are considerably improved in the presence of SnCl_4 .

Reaction Kinetics

The rate law for reaction 18 was determined, measured by initial rates of 2-benzene bromination. The effect of changing the HNO_3 concentration is illustrated in Figures 3 and 4. The effect of changing the 1-benzene concentration is illustrated in Figures 7 and 8. The reaction is first order in $[\text{Hn}]$ and approximately first order in $[\text{1-benzene}]$. High concentrations of 1-benzene inhibit reaction 18, as shown in Figure 9. High concentrations of SnCl_4 also inhibit 2-benzene production (vide infra).

The effect of changing the oxygen pressure above the solution is shown in Figure 10. The rate is independent of the oxygen pressure, a feature shared with the Br_2/O_2 co-catalyst system. The rate law is given in equation 19.

$$\text{rate} = k_1[\text{HNO}_3][\text{O}_2] / [\text{Hn}] = k_2[\text{SnCl}_4][\text{1-benzene}] \quad (19)$$

The temperature dependence of reaction 18 was also studied between 40 and 70°C , as shown in Figure 11. From the Arrhenius plot shown in Figure 12, the activation energy $E_a = 73.3 \text{ kJ mol}^{-1}$ was obtained. An activation energy $E_a = 78.3 \text{ kJ mol}^{-1}$ was reported for the Br_2/O_2 co-catalyst system.⁴⁵

Figure 2. Distribution of responses (total) with σ_2 in standard (left), $\sigma_2 = 0.001$ (middle), and $\sigma_2 = 0.0001$ (right).

[illegible]

1. *Journal of the American Medical Association*, 2000; 283: 2689-2696.

1000

Figure 1

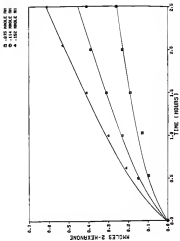


Figure 4. Calculation of square residues order to [10] for the automata transition to Figure 3.

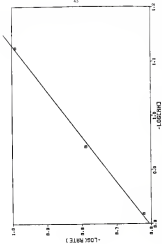


Figure 1. Reduction of 1-phenyl-2,3-dichloro-4,5-dimethyl-5-oxo-1,2,3,4-tetrahydronaphthalene (1) with SnCl_4 and SnCl_2 (10.00% solution) in ethanol (400 mL). Temperature is 60°C; pressure is 1 atm.

- Reduction 1, 2, 3, 4, 5-hexane.
- Reduction 1, 2, 3, 4, 5-hexane.
- △ Reduction 1, 2, 3, 4, 5-hexane.

Δ 100
 \square 200
 \circ 300
 \times 400
 \bullet 500

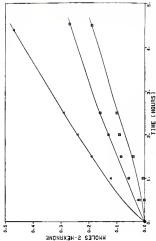


Figure 8: Calculation of apparent rate law order n_a (3-decades) for the reactions described in Figure 8.

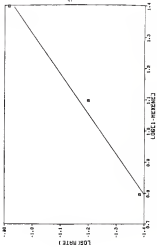


Fig. 3.3.3.3.3.3.3

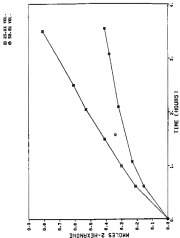


Figure 10. Collection of 3-isomers (13a) with O_2 and H_2O_2 (0.132 mmol) in ethanol (50 mL). Temperature = 40 °C.

- indicates 3a (1)
- indicates 3b (2)
- △ indicates 3c (1)

1000
 800
 600
 400
 200
 0

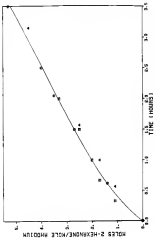


Figure 13 - Evaluation of 3-oxo- β -keto (13aL) with α , β - β (13aL), α , β - β (13aL), and β , β (13aL) using 13aL. β , β (13aL) = 13aL

13aL
13aL
13aL
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13aL

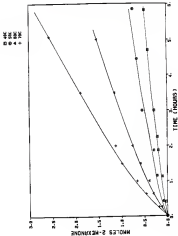
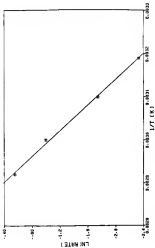


Figure 1b. Inclusion plot for calculation of inclusion weight
for the calibration described in Figure 5.



Griffin Isomerizations

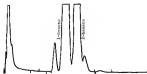
When EtCl_2 is used as the catalyst, extensive isomerization of 1-hexene to 2-hexene is observed by GPC, as shown in Figure 13. (This method does not distinguish between cis and trans isomers of 2-hexene.) This contrasts the Et_2Ti co-catalyst system, for which it was reported⁴⁹ that at the end of the reaction time of four hours, the amount of internal dienes was less than 10% of the expected terminal diene.

The fact that dienes are isomerized in the EtCl_2 system is not surprising, since EtCl_2 is known to catalyze an olefin isomerization catalyst.^{5,79} The active catalyst for this reaction is a rhodium(III) square olefin complex. Rhodium(III) square complexes are known to result from the reaction of EtCl_2 and primary or secondary alcohols⁸⁰ in the absence of copper and olefins, and this reaction is the basis for many synthetic preparations of rhodium(II) complexes.⁸¹

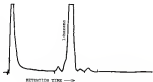
The fact that much of the terminal diene is isomerized in the EtCl_2 -catalyzed reaction may partially account for the decreased activity compared to the Et_2Ti co-catalyzed system. However internal dienes are obtained much more slowly by both EtCl_2 and Et_2Ti catalysts than are terminal dienes.⁴⁸

Figure 13. GC trace for the oxidation of 1-hexene (13aL) with O_3 and $h\nu$ (8.824 mW/cm²) in ethanol (13aL). Temperature = 40 °C, pressure = 48 psig. Samples were taken for analysis before and after reaction.

ARTERIAL INFUSION



VENOUS INFUSION



RETENTION TIME →

Acetone Production in Isopropyl Alcohol

The 50% selectivity of oxygen atoms for 2-butanone production found by Sgheri⁷¹ with 3.7×10^{-3} M SnCl_4 in the absence of Cu(II) suggests the concerted consumption of oxygen in four atoms. Thus the complete reduction of O_2 requires four electrons, and 2-butanone is providing only two, so that solvent must supply the remainder. This was demonstrated by employing 2-propanol as solvent, which produces acetone upon oxidation. The 1/1 acetone/butanone product profile shown in Figure 14 establishes the stoichiometry for the SnCl_4 -catalyzed alcohol oxidation shown in equation 18. The continuous formation of water during reaction 18 was detected by SnCl_4 but was not quantitated (vide infra).



At higher concentrations of SnCl_4 , acetone production increases relative to that of 2-butanone as illustrated in Table 1. This results from the SnCl_4 -catalyzed alcohol reduction of O_2 directly to H_2O (equation 19), as reported



previously.⁷¹ Sgheri points out that alcohol oxidation produces two species, which allow and drive production of water. The avoidance of peroxo formation may account for the consumption of both butanone and 2-butanone in the Sn/Cu system.

Figure 14. Qualitative of 1-bromo-11-hydroxy-12-methyl-13-oxo-14-oxa-15-undecanoic acid (14b) to 1-bromo-11-hydroxy-12-methyl-13-oxo-14-oxa-15-undecanoic acid (14c) in different pressure = 400 psi R_p .
 Q indicates methyl 3-oxooctanoate produced.
 Q indicates methyl 3-oxooctanoate produced.

□ 1.16 (3000 Å)
 ● 1.16 (2900 Å)

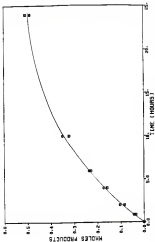


TABLE I
 ACTYNE AND 2-BUTYNE PRODUCTIONS FOR THE PdCl_2 -CATALYZED
 OXIDATION OF 1-BUTENE BY O_2 IN DIETHYLENE GLYCOL

run ^a	$[\text{PdCl}_2]$, M	mmol of actyne	mmol of 2-butyne	actyne/ 2-butyne mol ratio
1	0.0029	0.54	0.41	1.3
2	0.0037	0.79	0.77	1.3
3	0.0086	3.6	1.9	1.9
4	0.008	5.8	1.6	3.6
5	0.007	6.4	1.9	4.4

^aThese reactions were carried out at 40 psi and 40°C, with the appropriate amount of $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$, 4.44 mmol of 1-butyne (GAS Internal standard), 43 mL of diethylglycol, and 12 mL of 2-butanone. Reaction time was 24 h.

At high rhodium concentrations (10.004 M) the oxygen uptake also increases above the 2-bromo/2-bromosuccinic ratio reported by Syberg,²² as illustrated in Table 2. Syberg attributed this increase in succinic production relative to 2-bromosuccinic production to increasing temperature, but the fact that there is little change as the temperature is decreased from 50°C to 30°C implies that temperature is not a factor, but the rhodium concentration is.

Reaction 19 probably occurs via a metal-catalyzed decomposition of hydrogen peroxide (vide infra) which becomes more important at higher rhodium concentrations. Increasing $[RhCl_3]$ results in a decrease in reaction selectivity, which explains the poor selectivity with respect to oxygen desorption observed by Hines and co-workers with 0.01 M $RhCl_3$ as the catalyst.²³ Water has a deactivating effect on the $RhCl_3$ -catalyzed oxidation of alkenes,²⁴ and the continuous formation in both reactions 18 and 19 may be a factor in the catalyst deactivation. The rhodium/copper catalyst may have a longer lifetime because water is not formed in this reaction.

Water Production

As mentioned previously, the continuous formation of water during reaction 19 was detected by GLC, but was not quantitated. However, during the $RhCl_3$ -catalyzed 2-bromo oxidation in ethanol solvent, the amount of water present after 24 hours reaction time is substantially lower (measured

TABLE I
O₂ CONVERSION
FOR THE HgCl_2 -CATALYZED OXIDATION OF 1-BUTENE

exp ^a	$[\text{HgCl}_2]$, M	$[\text{BuCl}]$, M	T_{exp} , °C	Time, h	O atoms/ 2-butenes and water
1	0.0008	0.041	30	1.5	1.0
2	0.0008	0.042	30	1.5	1.0
3	0.0008	0.042	30	1.5	1.0

^aThese reactions were carried out in 60 ml with the appropriate amount of HgCl_2 (30.0, 0.35 mmol or 2-butenes (14.0 internal standard), 112 ml of solvent, and 30 ml of 1-butene.

re. as an internal standard) then after 2.3 hours reaction time, as shown below.

EtCl_2	$\text{Os}(\text{NO}_2)_2$	Δ_2 dicarboxylic acid peak area ratios		
0.0044 M		0.187(1 hr)	1.01(1.5 hr)	0.468(15 hr)
0.0042 M	0.0066 M	0.186(2 hr)	0.485(1.4 hr)	1.08 (24 hr)

This is not true of the corresponding Os/Ce catalyzed reaction, in which Δ_2 production appears to be continuous but slower. The substance used as an internal standard for ester measurement may be a poor choice, at least in the Os/Ce reaction. Eyring proposed⁷² that Os(II) catalyzes the slow combination of two carboxylic molecules to form dicarboxylic acids.

In the OsCl_2 system, a reaction which consumes Δ_2 occurs. This reaction could be derived by catalytic decarboxylation, as mentioned earlier. Alternatively, it is possible that at least some Wacker type olefin oxidation may occur in this system. Nolasco and co-workers proposed⁷³ a Wacker-type olefin hydroxymercuration as the second step in his mechanism. Nolasco and co-workers have also shown⁷⁴ that the complex $[\text{Os}(\text{2,2,6,6-tetramethylheptane})_2]\text{HP}_4$ will form two moles of 3-oxo-2-one per mole of rhodius in the presence of O_2 and HP_4 -diethyl ether complex as a proposed solvent (equation 24).



Et acetate is formed in this reaction. (Without $\text{HBF}_4 \cdot \text{OEt}_2$, one mole of 1-acetoxy-2-ene and one mole of H_2O per mole of product are formed.) This reaction is "slowly catalytic" in the presence of excess olefin. Thus, with 8 atoms of C_2 may be incorporated into ketone product even in the absence of Cu(II) . Wilson has suggested that the function of the strong acid is to protonate a $\text{Bu(III)}_{\text{ox}}$ complex to a Bu(III) oxonium complex, which may be capable of Wacker type catalysis. Some Ag^+ is present in this reaction, however (AgBF_4 is used to generate $[\text{Bu(1,7-octadiene)}]_2\text{BF}_4$ from $[\text{Bu(1,7-octadiene)}]\text{Cl}]_2$ (equation 17)).



Although AgClO_3 was found to be inferior to Cu(II) as a co-catalyst, it is possible that in any function is a similar fashion to copper in this model reaction, allowing both 8 atoms to be incorporated into ketone.

Substrate

Although ethanol (a primary alcohol) was generally the solvent used for this reaction, oxidation could be carried out on other primary, secondary, and tertiary alcohol substrates. The reaction is unsymmetrical (a secondary alcohol solvent is less active than is ethanol, as shown in Figure

15. Besides 1-bromocyclohexane, acetone is preferred as impregnant solvent (vide supra). Benzyl alcohol (a primary alcohol) may also be used as the solvent for reaction 15, producing 1-bromocyclohexane and benzylaldehyde (and other unidentified products).

Oxidation of 1-bromocyclohexane with KMnO_4 also occurs, and is exothermic, to 1-bromocyclohexanol (a tertiary alcohol), producing 4.3 liters in 15 hours. This is significant, since 1-bromocyclohexanol must be oxidized to a ketone as the primary and secondary alcohols. It implies that reduction of KMnO_4 to KMnO_2 need not occur for cyclic substrates. It does not rule out, however, such reduction occurring in primary or secondary alcohol solvents.

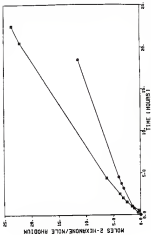
Alcohol Oxidation

Alcohols may be oxidized exothermically by KMnO_4 in the absence of aldehydes. Impregnant is oxidized to acetone, producing 13 liters in 24 hours. Similarly, 1-bromocyclohexane is oxidized to 1-bromocyclohexanol, producing 4.1 liters in 15 hours. Interestingly, the addition of copper(II) to the 1-bromocyclohexanol solution under identical conditions has no effect on this reaction. In this case 3.8 liters were seen in 15 hours. Thus, the presence copper(II) has little effect on alcohol oxidation by KMnO_4 in the absence of other substrates. Ryberg and co-workers have reported that copper(II) is capable of oxidizing at least some alcohols.^{72,73} Alcohols have been oxidized with osmium using OsO_4 and

Figure 15.

Reaction of 1-butene (1) with O_2 and NO_2 (0.05 atm). Temperature = 50°C, pressure = 1 atm, O_2 15, 1-butene 10, NO_2 0.05 atm.

(O) 2.0 mmole
 (●) 1.0 mmole



silver-silver ion.⁸² Copper(II) ion-exchanged T-mosilons have been reported to oxidize ethanol⁸³ and benzyl alcohol.⁸⁴

Effect of Acid

The effect of adding a strong acid to HClO_4 -catalyzed olefin oxidations was also studied and is illustrated in Figure 18. Acid (as H_2SO_4) has a strongly inhibitory effect on the reaction. This contrasts Hines and coworkers'⁸⁵ and Sperry's²² findings that when using HClO_4 peroxide, two equivalents of acid are necessary for maximum activity. It implies that the acid is required to form the active complex from a HClO_4 precursor, as Sperry has suggested.

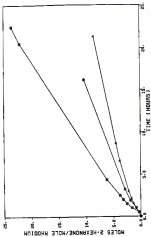
Since Hines and co-workers have reported²¹ that the addition of HBF_4 -diethyl ether complex (1 mole H^+ /mole olefin) to reaction 18 resulted in the utilization of both π bonds of dienes for ketone production, the addition of this acid to the HClO_4 -catalyzed 1-diene oxidation was studied. Because the HBF_4 complex is water-soluble, the water scavenger 3,3-dimethoxypropane was also added to this reaction. In this experiment, only 4.8 turnovers were observed in 4.8 hours (compared to 8.3 turnovers without HBF_4). The oxygen uptake was not measured in these experiments.

Effect of Radical Inhibitors

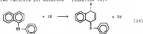
Although a free radical chain mechanism is not likely for the rhodium-catalyzed oxidation of olefins due to the

[illegible]

10 0.1-0.25
 9 0.25-0.5
 8 0.5-1
 7 1-2
 6 2-5
 5 5-10
 4 10-20
 3 20-50
 2 50-100
 1 100-200



specificity for 2-benzoic product and the low reactivity for 1-benzoic as a substrate, the effect of radical inhibitors on the system was investigated. The radical inhibitors used were 2,2,6,6-tetraphyl-1,3-dimethyl piperid (BHT) and 8-phenyl-1-o-naphthol (BPh). 8-phenyl-1-o-naphthol can react with two radicals per molecule²² (equation 18).

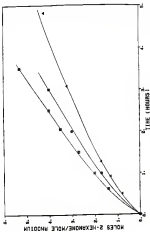


A 10-fold excess of BHT and BPh was each added to a BaCl_2 -catalyzed 1-benzoic oxidation. The results are presented in Figure 17. Although the initial rates appear to be slightly decreased in both cases, the observed behavior is not that expected of a free radical chain mechanism. Addition of a trap should lead to complete inhibition or an induction period if a free radical chain process is occurring. These results indicate that a radical chain process is not taking place, however, the presence of radicals is not excluded. Hyung²² has reported that initial rates of 1-benzoic oxidation by $\text{Ba}(\text{III})$ alone (generated in solution from $[\text{BaOCCl}_2\text{Cl}]_2$) are not affected by the addition of a 77-fold excess of BHT at 70°C . The decreased activity of the catalyst for 2-benzoic production may be caused by oxidation of the phenol trap by BaCl_2 in a competing reaction. Similarly, the same trap could contribute to BaCl_2 and compete for ligand sites on the metal.

Figure 17.

- Outcomes of 1-hour (1500) and 2-hour (3000) trials to obtain 50%¹ temperature = 50%² pressure = 50%³ ϕ .
- 1) Indicate in addition.
 - 2) Indicate 50% (0.50) value.
 - 3) Indicate 50% (0.50) value.

15 NO. COMPLETION
 16 100%
 17 100%
 18 100%



Ultraviolet-Visible Spectroscopy

The visible spectrum was monitored during the course of a 1-hour oxidation with O_2 at 45°C . The spectra obtained are shown in Figure 18. The catalyst $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in a solution of anhydrous cuprous in solution,²⁵ shows two low energy peaks at 493 nm and a shoulder peak at ~ 450 nm for BaCl_2 in ethanol (spectrum 1). When 1-hexene is added, these bands shift slightly to 491 nm and ~ 451 nm (spectrum 2). (These spectra were recorded in the presence of O_2 .) Spectra 3-6 were recorded in the first 60 minutes at reaction at 45°C . The low energy peak shifts progressively from 490 nm to a shoulder at ~ 450 nm. The feature at ~ 380 nm grows in intensity and may shift slightly. After 12.5 hours, only a shoulder at ~ 450 nm is seen (spectrum 6). The spectral changes may represent the loss of Cl^- from BaCl_2 in the course of the reaction. The visible spectra for copper-bromine rhodium(III) complexes in aqueous solution are well known. Pure chlorinated rhodium species have been shown to absorb visible light at progressively longer wavelengths.²⁶ Thus it appears that the BaCl_2 catalyst is being oxidized less gradually over the course of the oxidation reaction. It is likely that a mixture of several different rhodium species is present during and after reaction.

In Figure 18 is shown the result of the spectrophotometric titration of $\text{Ba}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in ethanol with progressively larger amounts of LiCl. These solutions were mixed and allowed to equilibrate at room temperature for 18 hours

100

the authors of the *Journal of Management Education* have been instrumental in the development of the field of management education. The *Journal* has been a leading voice in the field, and its authors have been instrumental in the development of the field. The *Journal* has been a leading voice in the field, and its authors have been instrumental in the development of the field.

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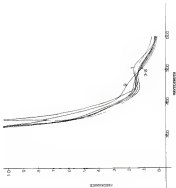


Figure 16. Spectrophotometric titration of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (10^{-4}M) with LiClO_4 in ethanol (total vol. 10 ml). Solutions were allowed to equilibrate for 30 mins at room temperature before the spectra were taken.





before spectra were taken. A shoulder peak is seen to grow in between 435 and 540 nm. This result confirms that rhodium species containing more chloride ion per rhodium atom at longer wavelengths than those containing less chloride ion in this non-aqueous system.

Rhodium(III) is reduced to rhodium(II) and (00) when solutions of RhCl_3 in ethanol are heated in the absence of H_2 . The solution color changes gradually from bright orange to yellow, and a finely divided black solid appears suspended in solution. This reaction has also been observed by visible spectroscopy. Such solutions are active catalysts for isobutene oxidation as oxidizers of ethylene and H_2 , but at much slower reduced rates. The solution color gradually becomes orange as oxidation products begin to form, but the black solid remains suspended.

The ESR spectrum was also recorded before, during, and after oxidation. Signals were removed from the reaction solution and the ESR spectra recorded. As seen in Figure 20, an axial signal is observed which exhibits a four-line hyperfine. In the spectrum, $a_{\perp} = 2.50$, $a_{\parallel} = 3.47$, and $g_{\parallel} = 1.98$. After reaction, the hyperfine is less distinct. In isopropyl alcohol, a similar signal is observed, with $a_{\perp} = 2.80$, $a_{\parallel} = 3.36$, and $g_{\parallel} = 1.98$. In an isopropyl solution (no β -hydrogen present), no signal is observed. Such signals are not characteristic of organic radicals, but of paramagnetic metal complexes.



This signal does not appear to be characteristic of a reaction species. For titanium, the (I) and (II) oxidation states are ESR-active. Further, the oxidized spin for titanium is 1/2. Thus, 2 equivalent or 4 inequivalent titanium (II) or (IV) metal would give rise to a four line appearance. No previous observations on this system or related systems have suggested this type of arrangement is likely.

This signal does appear to be characteristic of Ce(III) ($S = 3/2$, ESR-active). However, Ba/Ce -catalyzed oxidations give rise to ESR spectra that appear to be a superposition of two signals (Chapter II). The line intensities of the two signals were for the Ba/Ce oxidation system appears dissimilar to the signal observed here for the BaCl_2 system. As seen by comparing Figures 20 and 24 (Chapter II), the signal seen for the BaCl_2 system is less intense than that for the Ba/Ce system. It is unlikely that Ce contamination of either the titanium catalyst or the addition apparatus has occurred, since the unpropagated oxidation reaction exhibits no ESR signal. Further, aged solutions of BaCl_2 in acetone exhibit similar ESR signals (a_{H} = 3.08, a_{D} = 3.43, A_{H} = 120 G, 4-line hyperfine). Fresh solutions do not show an ESR signal. Thus, the origin of the ESR signal is uncertain, as are its implications.

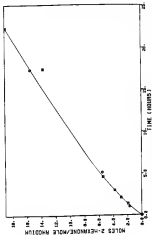
Effect of Oxygen Pressure

The effect of changing the catalyst pressure was also studied. Shown in Figure 12 is a comparison of 2-hour

Irradiation of L-histidine (100g) with γ in ethanol
 (400g). Temperature = 20°C, pressure = 1000 kg.
 Q (molecules/kg) (0 and 1000) constant.
 G (molecules/100g) (0, 0.04, 0.08) and 0.02 (0.04
 series, 1 series (1, 0.04, 0.08) constant).

Figure 11.

10 0000 1
 10 0000 1111 0001



oxidations made with HNO_3 and with $\text{Ru}(\text{NO})_2$ and HNO_3 (2 moles per mole of rhodium) as the catalyst precursors. There is no apparent difference in these oxidations. Thus, it seems that the rhodium(III) catalyst precursor has little effect on isobutane oxidation. Adams and co-workers have reported⁴⁵ similar behavior for the RuO_4 co-oxidized system. This is significant because it implies that the active catalyst is formed in solution equally well from different rhodium(III) complexes. Since rhodium(III) is substantially inert, a change of oxidation state before the active catalyst is formed is implied. Since there is no induction period for this reaction, this change in oxidation state must be rapid at 40°C (vide supra).

Sphery reports³² an induction period for isobutane oxidation when $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ is used as the precursor in the absence of a copper co-catalyst. The length of the induction period depends on the oxygen pressure, and the solution color changes from yellow to bright orange. Two equivalents (based on rhodium) of acid are required for maximum catalytic activity when using RhCl_3 precursors, both with and without a copper co-catalyst. Sphery has concluded that Rh(II) is oxidized to Rh(III) in the induction period, and that H^+ is necessary to generate a $\text{RhCl}_2\text{-O}_2$ intermediate. Adams and co-workers⁴⁶ also used a rhodium(I) precursor, $[\text{Rh}(\text{CO})_2\text{I}]_2$, and also reported the need for two equivalents of acid per rhodium, but did not mention if an induction period was observed in the absence of Cu(II) .

Effect of Chloride Ion

The effect of chloride ion on 1-octene oxidation was also studied. As illustrated in Figure 21, the addition of 1 mole of BaCl_2 per mole of BaCl_2 (the 1 mole equivalent of Cl^- per rhodium) has no effect on the 1-octene oxidation at 40°C (at least at low $[\text{Rh}]$). Since our co-workers have reported⁶⁸ that Cl^- is not necessary for catalytic activity with $\text{Rh}(\text{III})$ in the absence of $\text{Cu}(\text{II})$, $\text{Ba}(\text{ClO}_4)_2$ alone was found to be an active catalyst for 1-octene oxidation. The activity of $\text{Ba}(\text{ClO}_4)_2$ as a catalyst was reported to be five times less than the $\text{BaCl}_2/\text{Cu}(\text{ClO}_4)_2$ couple under the same conditions. The insensitivity of the $\text{Rh}(\text{III})$ only catalyst to chloride ion concentration confirms Moore's findings that is the Rh/Cu co-catalyzed system, five equivalents of chloride ion per rhodium give an inactive catalyst. It also confirms Tytner's findings⁷³ that is the BaCl_2 catalyzed oxidation at 70°C , five equivalents of chloride ion per rhodium causes greater catalyst stability.

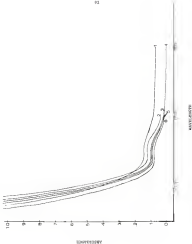
The visible spectrum was also monitored during the course of this oxidation with added chloride ion, and is presented in Figure 22. Although the broad shoulder peak at $720\text{m}\mu$ decreases in intensity as the reaction progresses, it does not shift to a lower wavelength, as is seen in the BaCl_2 -catalyzed oxidation without added chloride ion.

Since Moore and co-workers have proposed⁶⁸ that at least one function of copper in the reaction is to remove chloride ion from BaCl_2 , the effect of adding Ag^+ to an

Figure 10. Application of Johnson (1962) with R_0 as defined (1962). Temperature = 10°C. Assume a 50% R_0 .
 (1) Infestation 1800; (0.67% added) daily lay.
 (2) Infestation 1800; (0.67% added) not laid. (0.148 added) daily lay.



There are a number of reasons why the results of the present study may not be generalizable to other populations. First, the sample was relatively small and consisted of a convenience sample of students from a single university. Second, the study was cross-sectional and did not include a control group. Third, the study did not include a measure of social support, which is a known factor in the development of depression. Finally, the study did not include a measure of self-esteem, which is also a known factor in the development of depression. These limitations suggest that the results of the present study should be interpreted with caution and that further research is needed to confirm the findings.



active oxidation was studied. The results in Figure 24 show that addition of either 3 or 6 moles of Ag^+ per mole of RhCl_3 at the beginning of the reaction increases the initial rate somewhat. However, when Ag^+ is added in the middle of a RhCl_3 -catalyzed l-hexene oxidation, no increase in rate is seen as the Ag^+ is added. In all these reactions, a white precipitate of AgCl was observed in the reaction solution. The precipitate was not removed in these experiments. Although Ag^+ addition increases the initial rate, the catalyst is deactivated more rapidly, as shown in Figure 25. It is possible that Ag^+ may be capable of performing an overall sum of the functions of the copper co-catalyst. However, if the rhodium catalyst is not substitutionally inert (vide infra), the fact that additional Cl^- has no effect on RhCl_3 -catalyzed oxidations suggests that removal of Cl^- to form RhCl_2^+ is not as important for l-hexene oxidation as Ryberg has suggested.⁷¹

Figure 26 shows the effect of adding Ag^+ on the visible spectrum of RhCl_3 in ethanol (no visible substrate present). Immediately on adding at room temperature, the shoulder peak at $^{\circ}505$ nm seen for RhCl_3 is almost entirely shifted to $^{\circ}475$ nm. No precipitate was observed. After heating to 40°C for 20 minutes under O_2 with the spectra for RhCl_3 and the $\text{RhCl}_3/\text{Ag}^+$ solutions decrease in intensity, but the shoulder peak is not shifted in either case from the spectrum taken before heating. A new shoulder peak at $^{\circ}540$ nm is visible for the $\text{RhCl}_3/\text{Ag}^+$ solution. A precipitate is formed in this

1

[illegible]

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1. **Identify the problem.** The first step is to identify the problem. This involves understanding the symptoms and the context in which they are occurring.

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(●) 2: 1000/1000 (P-6, 1000)
 (○) 2: 1000/1000
 (▲) 4: 1000/1000

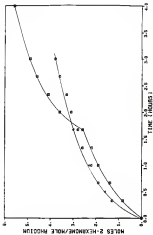


Figure 15.

Oxidation of tuberoses (100g) with O_2 and $HgCl_2$ (48,874 meq/l) in ethanol (40ml). Temperature = 40°C, pressure = 100psi.
O tuberoses are $AgNO_3$ added.
O tuberoses $AgNO_3$ 15,116 meq/l, 2 tuberoses (20) addition after 1-2 hours reaction time.
O tuberoses $AgNO_3$ 15,116 meq/l, 2 tuberoses (20) addition by replacement of oxygen.
+ tuberoses (20), 2 (20,116 meq/l, 4 tuberoses (20) addition at replacement of oxygen.

100 0 1000/2000
 100 0 1000/2000
 100 0 1000/2000
 100 0 1000/2000
 100 0 1000/2000

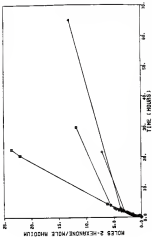
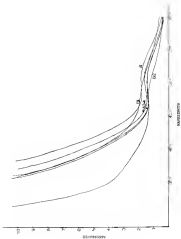


Figure 16-

Visible spectra for the reaction at 40°C. at:
A. 1821, 18.1000 before (a1) and after
(a2) heating.
B. 1821, 18.1000 and 1829, 18.1000 in ethanol,
before (b1) and after (b2) heating.



oxidation after heating which is presumed to be AgOH . Obviously the removal of chloride ion from RhCl_3 is difficult at low temperatures. It has been reported²⁸ that Ag^+ will not remove Cl^- readily. Our findings support the rapid reduction of rhodium(III) to rhodium(I) in ethereal solution even at room temperature.

Oxidants Other Than Dioxygen

Eyring reported²⁹ that H_2O_2 is an effective oxidant for both the RhCl_3 - and Rh/Cyclooctadiene -catalyzed isomerizations and that t-BuOOH is an effective oxidant for the RhCl_3 -catalyzed reaction. He reported that the order of addition was critical--if t-butanol was added to the reaction mixture before the oxidant, it would deactivate the Rh(III) catalyst by blocking coordination of H_2O_2 . He also reported that the tertiary alkylated t-butanol may be used as a solvent when peroxide oxidants are used, since an solvent reducing equivalents are necessary with the more highly reduced (compared to dioxygen) peroxide oxidant. These peroxide oxidations were further studied, to duplicate Eyring's findings and offer new insights.

The results are shown in Table 3. Several important conclusions may be drawn from these results. The order of addition is not critical, as Eyring states. The t-butanol may be added first, provided the solution is not heated under inert atmosphere for a great length of time before the oxidant is added. Such heating is the danger of catalyst

TABLE 3
 1-HEXENE PRODUCTION FOR THE SACI₂-CATALYZED
 OXIDATION OF 1-HEXENE WITH PERACIDS

Exptl Temp	Solvent	Cat.	1-Hexene Conc. Mole-%	1-Hexene Mole-%	Temperature (°C)
1	Hex	Ms	0.5000	1.00	30(20) 1.0(20) 1.4(40)
2	Hex	Ms	1.0000	1.00	30(20) .91(20) 1.0(40)
3	Hex	Ms	1.0000	1.00	30(20) .89(20) 1.0(40)
4	Hex	Ms	1.0000	1.00	30(20) .89(20) 1.0(40) 1.0(2.0)
5	Hex	Ms	1.0000	1.00	30(20) .88(20) .89(20) .89(40) .89(2.0) .89(1.0)
6	Hex	Ms	1.0000	1.00	30(20) .89(20) .89(20) .89(40) 1.0(2.0) 1.0(1.0)
7	Hex	Ms	1.0000	1.00	30(20) 1.0(20) 1.0(20) 1.0(40) 1.0(2.0) 1.0(1.0)
8	Hex	Ms	1.0000	1.00	30(2.0) 1.0(20) 1.0(40) 1.0(2.0) 1.0(1.0)
9	Hex	Ms	1.0000	1.00	30(20) .89(20) 1.0(40) 1.0(2.0) 1.0(1.0)
10	Hex	Ms	1.0000	1.00	30(20) .89(20) .89(20) 1.0(40) 1.0(2.0)
11	Hex	Ms	1.0000	1.00	30(20)
12	Hex	Ms	1.0000	0.60	30(20) .89(20) 1.0(40)
13	Hex	Ms	1.0000	0.60	30(20) .89(20) 1.0(40) 1.0(2.0) 1.0(1.0)
14	Hex	Ms	1.0000	0.20	30(20) .89(20)
15	Hex	Ms	1.0000	0.20	30(20) .89(20) .89(40) 1.0(2.0) 1.0(1.0)
16	Hex	Ms	1.0000	1.00	1.0(40) 1.0(20) 1.0(40) 1.0(2.0) 1.0(1.0)
17	Hex	Ms	1.0000	1.00	30(20) .89(20) .89(20) .89(40) 1.0(2.0) 1.0(1.0)
18	Hex	Ms	1.0000	1.00	30(20) 1.0(20) 1.0(40) 1.0(2.0) 1.0(1.0)
19	Hex	Ms	1.0000	1.00	30(20) .89(20) .89(20) .89(40) 1.0(2.0) 1.0(1.0)

reduce HbCl_2 to HbCl (vide supra), which reacts with HOOH slowly.

Ryberg also states that the reaction with peroxide is faster than that with O_2 . However, comparison of experiment 1 (performed under similar conditions, except in an O_2 atmosphere) with experiments 3-4 and 8-10 shows that the reaction rate is comparable with O_2 and hydrogen peroxide. Comparison of experiment 14 with 8-10 confirms however, that under similar conditions, the initial rate with 5- HOOH is about five times faster than that with HOOH , as Ryberg reported. The reactivity of various porphyrins with and allylthioetheroxides (TBOH) for oxidations catalyzed with metalloporphyrins has been correlated with the acidity of the leaving group ROH .⁸⁷

Increasing the $[\text{chlorine}]$ has little effect on the rate of the overall reactions obtained, as can be seen from a comparison of experiments 3-4 and 11-12. However, decreasing the $[\text{HbCl}_2]$ increases the overall percentage obtained, as is seen by comparing experiments 4-10 and 7. Increasing $[\text{HbCl}_2]$ greatly decreases the overall conversion, as is seen by comparing experiments 3-4 with 5.

Because Ryberg reports⁷² that conversion decreases with increasing initial $[\text{HOOH}]$, also, gradual addition of HOOH was made in attempt to increase the overall activity. This also addition resulted in lower conversion, as seen by comparing experiments 3-4 with 6 and 8-10 with 8. This indicates that the catalyzed peroxide decomposition is probably

and a source of peroxide ions. The incomplete reaction is probably due to catalyst deactivation. When 5.1 additional equivalents of H₂O₂ are added to experiment 18 after 2.1 hours, only 0.4 additional turnover are obtained.

As Sykes reported,¹² a solution of one 8-atom of peroxide is interpreted like 2-hexamers. Experiments 7 and 17 approach this estimate.

Although Haines noted that k_1/k_2 in the solution is the variable in the presence of O_2 , the effect of k_1/k_2 of an added oxidant in the absence of O_2 was studied. The results are presented in Table 4. The small amount of oxidation seen could result from trace oxygen in the solution. The solubility of O_2 in nonaqueous ethanol is $2.8 \times 10^{-3} M$. In the $SnCl_4$ -catalyzed 2-hexamers oxidation, formation of 0.013 moles of 2-hexamers (0.13 turnover in these experiments) would require 0.013 mole of O_2 . Under reaction conditions, the actual solvent used would have to exceed $3.8 \times 10^{-3} M$ O_2 . This exceeds the solubility limit for O_2 in ethanol slightly, but does not account for any O_2 present above the solution. The amount of O_2 present above the solution is a 25 cc round bottom flask resulting from not purging out any of the air in the flask is 0.21 moles. If a 12 cc flask is used, the amount is 0.013 moles. (Flasks 18 and 19 cc flasks were used in these experiments.) Thus, it would be possible to obtain the amount of oxidation observed in the experiments in Table 4 through improper purging if 1/18 of the air in the 12 cc flask remained above the nitrogen purge.

TABLE 4
2-HEXANE PRODUCTION FOR THE SnCl_4 -CATALYZED
OXIDATION OF 1-HEXENE WITH H_2O_2

Exptl	Solvent	Conc.	Water Spent Soln	2-Heptene wt. %	Temperature (Sec)
16	Hex	0%	—	1.30	.04 (.03) 1.30(.27) .04(.04)
17	Hex	0%	—	1.30	.04(.03)
20	2-PeP	0%	—	1.30	.05(.03) .04(.05) .05(1.7)
21	Hex	0%	16 g. H_2O	1.30	.05(.05) .04(.05)
22	Hex	0%	16 g. H_2O	1.30	.05(.05) .05(.05) .05(.05)
23	Hex	0%	40 g. H_2O	1.30	.05(.05) .05(.05) .05(.05) .05(.05) .05(.05)
24	Hex	0%	40 g. H_2O	1.30	.05(.05) .05(.05) .05(.05) .05(.05)

Reactions of S_2 -purged ethanol or other solvents were further purged for 30 minutes after addition to the reaction vessel (vide supra). [Specific volumetry failed to detect an oxygen wash in several prepared solutions prior to reaction.]

It is interesting that the greatest amount of oxidation (1/2 turnover) occurs in *n*-butanol, which will not reduce $Hg(II)$ to $Hg(I)$ (vide supra). This is apparent that $HgCl_2$ may be capable of Wacker-type oxidation, using water as the oxidant. In primary and secondary alcohol solutions, this reaction may not compete favorably with alcohol oxidation. The outcome observed in experiment 18 is interpreted as such and 0.40 turnovers after 2 hours, indicating almost complete conversion of $Hg(II)$ to $Hg(I)$.

To determine whether superoxide has played a role in the reaction, potassium superoxide was used as the oxidant under inert atmosphere. The gross ether dl -crown-4 was added to help solubilize EO_2^- . The EO_2^- appeared to decompose in ethanol solvent. In this reaction, 0.20 turnovers were observed in 1.7 hour, probably due to small amount of oxygen present from disproportionation of superoxide ion.

Triethylamine ($PhICl_2$) was also used as the oxidant to investigate the possibility of forming a radical(oid) as complex, which could undergo Wacker-type oxygen transfer in ethanol as suggested by Minami and co-workers.¹⁰ This reaction was conducted under S_2 at $44^\circ C$ in ethanol solvent, similar to the experiments using $HOCl$ as oxidant. The

Isobutylenes are isochlorogenic with 1-butene. After 4.4 hours, 1.8 turnover are observed. Thus Rh(III) system is incapable of oxidizing 1-butene with PAB in a stable active species.

It has been reported that PAB is unstable in alcohol solvent, undergoing a solvolysis reaction^{10,11} (equation 19).



A second 5-atom transfer reagent, para-oxo-3,5-dimethyl-oxoline B-oxide^{10,11} (p-OM-OMAO), was also used as the oxidant in this system, since it does not react with alcohol solvent. With $RhCl_3 \cdot 5H_2O$ as the catalyst in alcohol solvent under H_2 at $40^\circ C$, only 0.14 turnover are observed in 4.2 hour.

Isobutene Reaction

The incorporation of a deuterium label from alcohol solvent CD_3OD was studied to investigate possible chain sequence in the $RhCl_3$ -catalyzed 1-butene oxidation with B_2 . For example, the decomposition of a germacolenylrhodium, **4**, through hydride elimination as catalyzed by Rhodium would result in a completely deuterated product, CD_3CHO .



Especially, decomposition of 3 via a β -ketone-elimination (equation 10) could result in the desired product CH_3COCH_3 . Other similar decomposition paths may also be envisioned (equation 11). Decomposition of an acylpyranone-rhodium species, 3, would also result in CH_3COCH_3 .



Decomposition of a hydronitrated acylpyranone intermediate in a Baeyer-type step would be expected to proceed via a semi-initiated hydride shift. An unimolecular ketone would result.

It is expected to frequent to the next section—where we show below,



The results shown in Figure 27 indicate that overall 3-4 deuterium atoms are incorporated into 3-hexanone product by comparison of the parent ion peaks at m/e 204 and 140 with that for unsubstituted 3-hexanone at m/e 100. In the homoethyl methyl group, 1-2 deuterium atoms are incorporated, as seen by comparing the peaks for the methyl fragment at m/e 44-46 with that at m/e 43 for the unsubstituted 3-hexanone. On the carbon adjacent to the methyl, 1-2 deuterium atoms are incorporated, as seen by comparing the peaks at m/e 57-59 with that at m/e 45 in the unsubstituted 3-hexanone. This result is not surprising in light of the observation that 3-hexanone isomerization in this system is selective.

Figures 28 and 29 show deuterium incorporation into the substrate 3-hexanone and the 2-methylpentan-3-one internal standard. The extensive deuterium incorporation in 3-hexanone results from the random catalyzed isomerization. The fact that scrambling occurs on the 2-methylpentan-3-one indicates that equilibration of methyl ketones is occurring. Overall 5 deuterium atoms are incorporated into 3-hexanone, as seen by comparing the parent ion peak at m/e 101 with that at m/e 100 for the unsubstituted 3-hexanone. Of these, 2-2 deuterium atoms appear to be the terminal methyl group (m/e 45-46

Figure 37. Reaction of 1-benzo (LBM) with O_2 and H_2O_2 (8.187 mmol) in dimethyl sulfoxide (DMSO). Temperature = $40^\circ C$, pressure = 60 mmHg H_2 . Reaction samples were compared with unlabeled compounds.

1-HOURING CONTROL

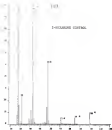


Figure 18. Oxidation of 1-hexene (18aL) with O_2 and K_2O_2 (0.1M serial) in decahydral nitroal (43aL). Temperature = 60°C, pressure = 48psig O_2 . Reaction complex was compared with Redox-catalyzed complex.

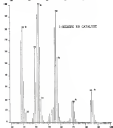
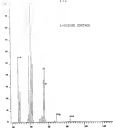
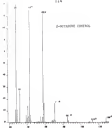


Figure 29. Oxidation of 1-benzene (13a) with H_2 and HCl (0.187 mmol) in deuterated ethanol (5a). Temperature = 42°C, pressure = 40 atm H_2 . Reaction couples were compared with determined compounds.



rs, 43), and 1-2 on the carbon adjacent to the carbonyl (c/a 87-88 vs. 85).

Other Studies

Carbon monoxide was added to an active solution to observe the effect. As shown in Figure 30, reaction stops almost immediately upon CO addition. Carbon monoxide is reported to bind strongly to Rh(I) , which would retard olefin coordination. However, this does not necessarily imply that the active species for olefin oxidation is a Rh(I) species. Rhodium(III) halides have been reported to react with CO in aqueous acid solutions^{32,33} and dimethylacetamide³⁴ to produce $\text{Rh(III)}(\text{CO})_2^+$ and CO_2 . A $\text{Rh(III)}\text{CO}$ intermediate has been isolated in this reaction. The Rh(I) chloroethyl may be oxidized with O_2 back to $\text{Rh(III)}\text{CO}$ and CH_3Cl . Thus, a catalytic cycle for oxidizing CO is possible. The visible electronic absorption spectrum of a RhCl_3 catalyzed 1-octene oxidation taken after CO addition is similar to that for $[\text{Rh}(\text{OH})_2\text{Cl}]_2$.

The reaction between RhCl_3 and 1-octene was also studied.³⁵ The ESR spectrum of a solution of 3.0M 1-octene in CH_2Cl_2 (1.4M) in d_2 -methylene (9.3 wt) was recorded, and is shown in Figure 31. Bicyclopentadiene (1.4M) was added to the solution as an internal standard. In Figure 31a, the resonance at 1.1 ppm is due to the tertiary butyl protons in 1-octene, the resonance at 2.45 ppm is due to the tertiary butyl protons in 1-octene, and the resonance at 3.45 ppm is

Figure 10.

Derivation of 3-benzenes (3Sb) with δ_1 and 3Sb, 10-ata
model (a, abbas, Cited). Transformation = $\frac{100}{100}$
process = 100% δ_1 .
a) Definition of 100 added.
b) Definition 100 added after 3.8 hours.

100% CH₂
 100% CH₃

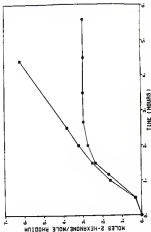
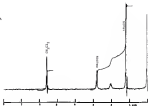
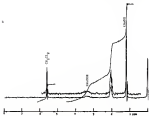


Figure 51. ^1H NMR spectra of:
 A. 1.0M HAcOH in H_2O (1 L) in $\text{d}_2\text{-}$
 acetone (8, vol.) , with CH_2Cl_2 (2 L)
 as internal standard.
 B. A 50/50 volume mixture of the
 sample in A with H_2O (0.01M) in
 $\text{d}_2\text{-acetone}$.

a.



b.



due to Et_2SiCl_2 . This solution was added with an equivalent solution of SnCl_4 in d_4 -acetone. The NMR spectrum was again recorded and is shown in Figure 11B. The peak at 1.83 ppm due to EtSiOSn broadens and almost disappears. However, integration shows that the peak is still present. Further, the ratio of the peak areas of each the 1.2 ppm resonance (EtSiOSn) and the 1.83 ppm resonance (EtSiOSn) to the internal standard does not change upon addition of SnCl_4 . Thus it appears that EtSiOSn coordinates to $\text{Sn}(\text{IV})$ rapidly in solution. Coordination of ligands to metal species often shifts the ligand NMR resonance. However, no other (isolated) peaks were obtained either upfield or downfield. Coordination of ligands to paramagnetic metal species often broadens the NMR spectra, however $\text{Sn}(\text{IV})$ is not paramagnetic.

To investigate the possibility that species are involved as intermediates in the SnCl_4 -catalyzed L-homocoupling reaction, the conversion of species in between with SnCl_4 was investigated. Another SnCl_4 and $(\text{EtOCH}_2\text{Si})_2$ converted 1,2-epichlorohydrin to ethyl vinyl ether in ethanol solvent at 40°C .

Characterization of Isolated Catalyst

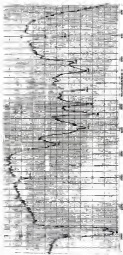
Spent catalyst was recovered from a reaction with a high concentration of SnCl_4 (8.02 M) by removing the solvent and heating with a excess unreacted ester solution was complete (48 hours). The dark red-brown solid obtained was dried under vacuum at 120°C . The infrared spectrum,

reported as a liquid salt, is shown in Figure 11. The IR spectrum differs considerably from that for $\text{BaCl}_2 \cdot 12\text{H}_2\text{O}$, for which there is essentially only one absorbance, a strong band at 325 cm^{-1} due to H-O-H stretching. In the spent catalyst, new absorbances appear at 2000, 1713, 1380, 1260, 1100, 1035, and 850 cm^{-1} . The strong band due to H-O-H stretch is also present.

Assigning these bands is difficult. In general,²⁴ coordinated H_2O has bands at 340-450 cm^{-1} (rocking mode). Ethylenic complexes exhibit an absorption below 1300 cm^{-1} due to H-O-H bending mode. Bridging OH groups show a band near 1100 cm^{-1} due to H-O-H bending in the IR spectrum of a Cu(II) complex having bridging OH groups.²⁵ All of these are possible ligands on the deactivated Ba(II) catalyst.

Ethylenic complexes generally exhibit a strong and sharp metal-ethylene stretching band between 1350 and 1700 cm^{-1} ²⁶. Terminal H-Cl stretching bands appear at 400-500 cm^{-1} . Bridging H-Cl stretching frequencies are lower than terminal H-Cl stretches. Metal alkoxides generally exhibit C-O stretches at about 1000 cm^{-1} and H-O stretches below 400 cm^{-1} . Symmetrical aldehydes (acrylates) exhibit C=O stretching bands near 1650 cm^{-1} . This band is shifted on coordination to a metal. For example, in 1604 cm^{-1} in a Pt(II) complex. Again, any of these ligands or the deactivated catalyst may be a mixture of complexes.

Figure 12. 3D rendering of the agent path, overlaid between 2000 and 4000, rendered as a light red.



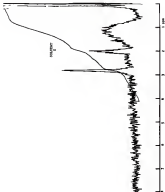
The ^1H NMR spectrum of the typical catalyst is 4-chloro-*para* was also recorded,²⁵ and is shown in Figure 13. While $\text{BaCl}_2 \cdot 10\text{H}_2\text{O}$ shows no peaks in the ^1H NMR spectrum, the unreacted catalyst shows broad peaks in the 0.5-2 ppm range (CH_2 -type protons) and a broad peak at 2.8 ppm (perhaps an unreacted species). A peak at 8.1 ppm may be a side band or due to solvent stopped glass.

The uv-visible electronic absorption spectrum of BaCl_2 reaction solutions after reaction shows no peaks in the visible region. However, the IR spectrum (this paper) indicates that chloride has not been completely removed from the reaction complex. It is possible that a mixture of reaction species is present after reaction.

Szyng¹² reports that fresh inactive BaCl_2 reaction solutions are a deep green in color, in contrast to the orange color of active solutions. He suggested that this color may result from intermolecular charge transfer in a complex having one thin and one wide center. Thus, Szyng suggested bimolecular species- or non-bridged $\text{Ba}(\text{Cl})_2$ dimers were present in inactive catalyst solutions. The solutions were IRF white.

The addition of ethyl ether to a spent catalyst reaction solution yields a white precipitate which redissolves in ether separating free solution. The white precipitate was not assigned.

Figure M. 1g. 100 specimens of the spot *Leiostomus xanthurus* collected in 1962.



Other RuCl₂ Catalyzed Oxidations

Several other related metal catalyzed oxidations were attempted. The oxidation of isopropyl with RuCl_2 (0.01M B) was conducted at 40°C under 1 atm O_2 . Two equivalents of H^+ (based on ruthenium) as HClO_4 were also added. In this reaction 2 isomers were observed after 2 hours. This is somewhat slower than the oxidation of 2PHE with RuCl_2 (no acid added), which produces about 3 isomers in one hour.

The isopropyl oxidation of 1-octene with O_2 or H₂O₂ was attempted with $\text{Ru}(\text{PPh}_3)_4\text{Cl}_2$. Both reactions were run at 40°C . With isobar solvent, only trace amounts of 2- and 3-octenes were observed. With O_2 , a peak was observed growing in size with time under the alcohol solvent GC peak. This peak was not identified. It has been reported⁴² that $\text{RuCl}_2(\text{PPh}_3)_3$ with various 1-octenes and styrene in various solvents. Chlorinated hydrocarbons solvents were proposed to assist in forming the active catalyst, a ruthenium hydride. Hydrogen peroxide can be decomposed catalytically by this complex.

The $\text{Ru}(\text{PPh}_3)_4$ -catalyzed oxidation of PPh_3 with O_2 was attempted in isopropyl solvent at 40°C and 40 psi O_2 to determine if alcohol oxidations would occur. Little or no octene was produced in this reaction.

Catalytic Mechanism

The catalytic cycle proposed for the RuCl_2 -catalyzed alcohol olefin oxidation by O_2 is shown in Figure 24. This

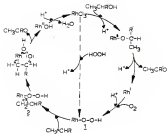


Figure 18. The mechanism for the RhCl_3 -catalyzed oxidation of 1-benzenes with H_2O_2 and SO_2 .

mechanism incorporates all the reported features of this reaction. Alkyl reduction of diorganics to a rhodium-cyclo-
 oxidized hydroperoxide complex is proposed in the first half of
 the cycle. This probably proceeds via a two step process
 involving the two successive alkyl reductions of RhCl_2 and
 the final complex of the resulting RhCl or rhodium hydride
 complex with O_2 to form RhOOH . Rhodium trichloride complexes
 have been shown to be capable of oxidizing primary alcohols
 to aldehydes and secondary alcohols to ketones,^{78,80,94,95}
 with the subsequent formation of rhodium hydrides.

Rhodium(II) complexes have also been shown to
 oxidize alcohols to ketones,^{100,101} with reduction of O_2 to
 H_2O_2 . Rhodium hydroperoxide species are known to result
 from the insertion of O_2 into a Rh-H bond,^{1,102,103,104}

Alternatively, intermediate 1 may result from protona-
 tion of a rhodium peroxo complex. This hydroperoxide complex
 may also be formed via the direct reaction of rhodium(III)
 with HOOH , as indicated by the dashed line in the cycle of
 Figure 14. The reaction with HOOH circumvents that part of
 the cycle in which alcohol oxidation and reaction with O_2
 generates RhOOH . The coordination of HOOH to Rh(III) has
 been reported in the preparation of $\text{H}_2[\text{Rh}(\text{Cl})_2\text{H}_2\text{O}(\text{OOH})]$.¹⁰⁵
 The intercalation of RhOOH to RhCl_2 has also been demon-
 strated (vide supra).

The coordination of the peroxo group to a rhodium(III)
 (or other high valent group VIII metal) rather than a Rh(II)
 species is recognized^{13,16} as being too distinguishing

properties. First, the oxygen of the peroxide is more weakly bound to the rhodium(III) complex, so it maintains more nucleophilic character. Second, the group VIII metal complexes may coordinate alkenes, bringing them into the proximity of the peroxo group. As a result, the lactonized $\text{RhCl}_2\text{CH}_2\text{COOH}$ is produced. A reagent of this compound is configurationally not to transfer a hydride ion to rhodium(III) and decomposes to lactone by proton transfer to the terminal carbon atom. If either the formation or decomposition of the intermediate formed in this way is considered rate limiting, a steady-state treatment of this mechanism predicts a first order dependence of the rate law on $[\text{RhCl}_2]$ a reaction order in $[\text{1-hexene}]$ which approaches first order at low $[\text{1-hexene}]$, and a zero order dependence on $[\text{O}_2]$.



$$\text{rate} = k_2[\text{Rh(III)OOH}][\text{CH}_3\text{CH}_2\text{H}] \quad (16)$$

$$\frac{d[\text{Rh(III)OOH}]}{dt} = 0 = k_1[\text{Rh(I)}][\text{O}_2][\text{H}^+] - k_{-1}[\text{Rh(III)OOH}] \quad (17)$$

$$[\text{Rh(III)OOH}] = \frac{k_1[\text{Rh(I)}][\text{O}_2][\text{H}^+]}{k_{-1} + k_2[\text{CH}_3\text{CH}_2\text{H}]} \quad (18)$$

$$\text{rate} = k_2 k_1 \frac{[\text{Rh(I)}][\text{O}_2][\text{H}^+][\text{CH}_3\text{CH}_2\text{H}]}{k_{-1} + k_2[\text{CH}_3\text{CH}_2\text{H}]} \quad (19)$$

$$\begin{aligned} \frac{d[\text{Co}(\text{II})]}{dt} &= 0 = k_1[\text{Co}(\text{II})][\text{Co}_2(\text{CO})_8] - k_{-1}[\text{Co}_2(\text{CO})_8][\text{Co}(\text{II})] + k_2[\text{Co}(\text{II})][\text{Co}_2(\text{CO})_8] - k_{-2}[\text{Co}_2(\text{CO})_8][\text{Co}(\text{II})] \\ &= k_2[\text{Co}(\text{II})][\text{Co}_2(\text{CO})_8] - k_{-2}[\text{Co}_2(\text{CO})_8][\text{Co}(\text{II})] \end{aligned} \quad (40)$$

$$[\text{Co}(\text{II})] = \frac{k_1[\text{Co}(\text{II})][\text{Co}_2(\text{CO})_8]}{k_{-1}[\text{Co}_2(\text{CO})_8][\text{Co}(\text{II})] + k_2[\text{Co}_2(\text{CO})_8]} \quad (41)$$

$$\text{rate} = k_1 k_2 \frac{[\text{Co}_2(\text{CO})_8][\text{Co}(\text{II})][\text{Co}_2(\text{CO})_8]}{k_{-1} + k_2[\text{Co}_2(\text{CO})_8]} \quad (42)$$

In this steady state treatment, it was assumed that reaction 34 is rate-controlling, reaction 32 is not reversible, and reaction 35 is irreversible.

The mechanism proposed in Figure 34 is similar to those suggested for the $[\text{CF}_3\text{CO}_2\text{Pd}(\text{n-decyl})_2]_2$ -catalyzed *n*-decyl oxidation of olefin to 2-butenes in 80% yield³³ and the $\text{Pd}(\text{OAc})_2$ -catalyzed Wacker oxidation of olefin to the same product.³⁵ In the former system it was found that the carboxylate bridging ligand, RCO_2^- , has a strong influence on the catalytic activity of the palladium complex, with the more electron withdrawing carboxylate ligands creating more active catalysts. For example, CF_3CO_2^- produces a catalyst 100 times more active than does CH_3CO_2^- . Thus increasing the Lewis acidity of the $\text{Pd}(\text{II})$ complex considerably enhances its effectiveness for the catalytic oxidation of 1-butenes to 2-butenes. The similarity between the product specifications found for the terminal olefin oxidations catalyzed by $[\text{CF}_3\text{CO}_2\text{Pd}(\text{n-decyl})_2]_2$ with *n*-decyl, and for the $\text{RhCl}(\text{PPh}_3)_3/\text{Co}(\text{II})$ species with O_2 as oxidant, was explicitly mentioned by the report on the palladium complex catalyst. Both of these reactions produce 99% 2-butenes from the

peroxide oxidizing equivalents [see for t -BuOOH, *ibid.* for H_2].

The isomerization of l -lysine observed in this system is expected in the context of our proposed mechanism. As pointed out earlier, in ethereal solvents, $HgCl_2$ is well known as a classic isomerization catalyst.² The mechanism of this reaction has been studied extensively¹⁸⁵ and involves a rhodium (III) hydride olefin complex. Isomerization proceeds by an addition-elimination mechanism. The fact that l -lysine isomerization occurs in the $HgCl_2$ -catalyzed oxidation implies the presence of hydride rhodium(III) complexes. The observation that isomerization occurs to a much lesser extent in the Hg/Cu system suggests that if rhodium species are formed (by promotion of a $Rh(I)$ complex), they undergo rapid redox reactions with $Cu(II)$ to form $Rh(III)$ and $Cu(I)$ (Chapter 3).

The increased acetone production relative to l -lysine at high $[HgCl_2]$ described earlier may be explained in the context of the proposed mechanism. As $[HgCl_2]$ increases, the peroxide concentration is reduced, inasmuch as well, a metal-olefinated decomposition of peroxide results in the formation of H_2O . This increasing peroxide decomposition at higher concentrations of rhodium olefinated accounts for the inefficient utilization of H_2 in the rhodium-olefinated reaction reported by Shono and coworkers.⁴⁸

Alternatively, it is possible that the decoupling alcohol oxidation reaction is suppressed and unreacted α -olefin

oxidation. The fact that several isomers of 2-benzenes produced are obtained in 2-benzal oxidations suggests that solvent reduction of Sn(II) is not necessary for complete activity. A mechanism may be envisioned in which a Fischer-type hydroxylation of aldehydes occurs initially. Sn(II) could be produced in this reaction, which could regenerate O_2 and further oxidize in a manner similar to that described by Kimm and coworkers.¹⁸

Further, Ryberg's SnCl_2 -catalyzed 2-benzenes oxidations at 70°C ¹⁹ are worth noting. In these reactions, 2-benzenes production was significantly slower than 2-benzal was produced in the first hours of reaction. This implies that another competing reaction may be important as temperature is increased, possibly the Feter-Wiles decomposition of peroxide intermediates, from which 2-benzenes might reasonably be formed. In the 2-benzenes oxidation at 45°C , no 2-benzenes is detected by GC-MS.

Ryberg also reported that at 70°C the oxidation of 2-benzenes was second order in SnCl_2 (equation 18). However, the competing alcohol oxidation is even more favored as temperature is increased, as shown by the copper uptake, and this may interfere with the determination of the reaction order in rhodium.

Mechanisms which involve free radical species, such as Feter-Wiles decomposition of alkyl hydroperoxides do not likely play a large role in SnCl_2 -catalyzed 2-benzenes oxidations since radical inhibitors had little effect on the

lateral race. Sjöberg has also reported that the addition of SnCl_4 does not affect the induction period or lateral reaction rate when $[\text{Rh}(\text{OAc})_3(\text{Li})_2]$ was used as the catalyst precursor.

Catalyst Deactivation

The deactivation of the RhCl_3 catalyst for *l*-lysine oxidation appears to be accelerated by several factors. Water is known to inhibit the catalyst-coordination to be formed in the RhCl_3 reaction. The lifetime of the catalyst appears to be related with H_2O_2 instead of O_2 as the oxidant. (In fact, Minoura and co-workers note that the addition of small amounts of H_2O_2 to a $\text{Rh}(\text{III})/\text{Sn}(\text{II})$ catalyzed *l*-lysine oxidation with O_2 inhibits catalytic activity.⁴⁰)

The catalyst seems to deactivate at high rhodium concentrations. Deactivation mechanisms which are second order or higher in rhodium concentration, for example the formation of one or hydrogen bridged rhodium species, may be more important at high rhodium concentrations. Minoura has reported that the white polynuclear di- μ -hydroxo complex,

$[\{\text{Rh}_2\text{F}_2\}_2\{\text{Pd}(\text{OAc})_2\text{Pd}(\text{PPh}_3)_2\}_2\{\text{PF}_6\}_2]_{12}$, forms from $\text{Pd}(\text{PPh}_3)_2/\text{H}_2\text{O}_2$ in the presence of water and $\text{SnF}_4 \cdot 8\text{H}_2\text{O}$, and is inactive for olefin oxidation.⁴⁸

Sjöberg and co-workers have reported that with isolation of $\text{Rh}(\text{I})$ complexes bound on a silica polyorganosiloxane support improves catalyst lifetime.^{72,78} Further, they showed that $[\text{Rh}(\text{Cl})_2\text{H}_2\text{O}(\text{OAc})_2]$ is inactive as a catalyst precursor for *l*-lysine oxidation.

However, it may be that competing reactions are favored at high catalyst concentration due to higher reaction orders in reagents. While the Rh(III) catalyst may no longer oxidize 1-hexene, it may still be capable of oxidizing alcohol. Further, 1-hexene, formed from isomerization of 1-hexanol, is unreactive in the oxidation.

Spectral observations of the catalyst during and after reaction indicate that Cl^- loss occurs gradually during the reaction. However, the chloride concentration seems to have less effect in the RhCl₃ system than with the Rh(III)/Cu(II) co-catalyst. The deactivated catalyst appears to coordinate an organic ligand, and possibly hydride and bridging are no hydrous ligands. Such bridged dimers are known to occur. For example, in hydrous oxidation by a Cu-O₂²⁻ peroxo-species complex, the bridged two Cu-O₂-Cu aggregate is not an active catalyst.⁴⁶ In our system, it is possible that several different Rh(III) complexes comprise "deactivated" catalyst.

CHAPTER 3
THE MECHANISM OF THE HYDROLYTIC OXIDATION OF 1-BUTENE
BY $\text{H}_2\text{O}_2/\text{Cu}(\text{II})$

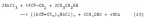
Background

Both Eyring²² and Hines and co-workers²³ presumed that the HClO_2^- and $\text{H}_2\text{O}_2/\text{Cu}(\text{II})$ -catalyzed 1-butene oxidations are fundamentally similar. Thus, the kinetics of the $\text{H}_2\text{O}_2/\text{Cu}$ system draws heavily on the HClO_2 reaction.

The most striking differences in the presence of copper (as loan) co-catalyst are the greatly increased activity, the incorporation of both 2- and 3- into 1-butene product, and the comparatively slight extent of olefin isomerization²³ (Chapter I). Thus, it appears that copper does play a direct role in the reaction.

The most obvious role for copper is the generation of less chlorinated radical species. Hines and co-workers have reported²³ the production of CuCl in the early stages of the reaction, which may be isolated in "100% yield from the reaction mixture with an apparent 100% yield from the reaction mixture with an apparent 100% yield. The remaining 10% is presumably soluble and is available for reaction. Also in the early stages of the reaction, approximately equimolar (with radical) amounts of acetaldehyde

(produced from ethanol solvent oxidation) are detected, indicating the reduction of Rh(III) to Rh(I) (equation 43).



This Rh(III) reduction would also explain the inhibitory effect of chloride ion and the observed oxidation acidity. Acetone, when exchange with reduction of Cu(II) must come to produce CuCl. Thus, a coordination of ethylacetone(1) by Cu(II) would produce Cu(1) and Rh(III). Hansen and co-workers suggest⁸⁵ that Rh(III) is again reduced via reaction 41 to produce a catalytic Rh(I)-diethyl complex. The overall reaction is shown in equation 44.



Thus, if the copper to rhodium ratio is 1:1, 3/2 equivalents of acetaldehyde would be produced in the simultaneous reduction of rhodium(III) to rhodium(I) and copper(II) to copper(I).

Byrnes⁸² also studied the inhibition step to produce CuCl. In one experiment, conducted in isopropanol solvent (because the oxidized product acetone is somewhat easier to remove than acetaldehyde), using a copper to rhodium ratio of 1:1, 1 1/2 equivalents of acetone is formed (based on rhodium) immediately on stirring, and stops constant for at least

30 minutes. Based on these results, Syberg concluded that a simultaneous reduction of rhodium(III) and copper(II) was ruled out, and that only copper(II) was reduced to copper(II), according to equation 45.



Syberg also suggests that such a chloride ion removal is not facile. An initial reduction of Rh(III), inhibiting chloride ion, may occur.

However, Syberg obtained similar results with both Fe(III) and Fe(II) salts, producing the same quantity of acetone.⁷² These results were inconsistent with a proposed reduction of only the co-catalyst.

Blanco and co-workers⁷ used active catalysts⁵⁹ containing a total ratio of 5 chloride ions per rhodium, whether rhodium(III) or rhodium(II) be used as the catalyst precursor. A total of 5 chloride ions per rhodium has no inhibitory effect on the reaction. This contrasts the RhCl_3 -catalyzed reaction, which does not appear to be sensitive to the amount of Cl^- present (Chapter 2). Syberg⁷² reports that at 70°C, a total of 5 Cl^-/Rh gives mild stability to the catalyst, with only a small inhibition of the initial rate. Syberg also suggests that the removal of chloride ion from Rh(III) in the initiation step may account for the 50-fold increase in initial rates and improved specificity for the Rh/Ce system. This, however, is unlikely in light of the

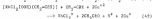
Investigation of the effect of chloride ion presented in Chapter 2.

Sykes also notes⁷² that as chloride concentration in solution is decreased at 40°C, maximum activity is obtained with a Cu/Fe ratio of 1:1. This maximum Kinoshita and co-workers⁶⁹ report⁶⁹ that initial rate is proportional to copper concentration only below a Cu/Fe ratio of 1:1. Further, as temperature is increased to 70°C, a Cu/Fe ratio of 2:1 is reported by Sykes to give maximum rate.

Kinoshita and co-workers⁶⁹ suggested that copper may provide some function and may act as a transient O_2 carrier, although neither of these possible roles were elaborated. Sykes⁷² assumes a role for Cu(I) in reducing O_2 to cuprous peroxide, $Cu_2O_2^{+2}$, which reacts with $HgCl_2^{+2}$ to form the active catalyst (equations 45-47).



Copper(I) is reformed in the cycle according to equation 46.



Thus, the expected reduction of O_2 to peroxide is suggested, through the indirect use of chemical reducing equivalents provided in the initiation step. This proposal avoids the need for exact estimates of O_2 as seen in the $HgCl_2$.

assigned reaction because silver provides reducing equivalents for the Cu(II)/Cu(I) cycle in the step forming the second mole of ketone. The intermediacy of peroxide is suggested by the similarity of the oxidation with H_2O_2 as the oxidant. However, even in the Hg(II)/Cu(II)-catalyzed 1-ketone oxidations with peroxide, a mixture of one 3-mole is incorporated into 2-ketone product (vide infra).

No direct evidence has been reported for copper's role in the reaction. Ryberg's proposed intermediate $[HgO_2(CHO)(CHO_2-CH_2)]$ is similar to Silver and co-workers' $[HgO_2(CHO_2-CH_2)]^+$ in its formation and then decomposition of a peroxopentacycle. Ryberg does not specify how the reaction proceeds once this intermediate is formed.

In this chapter is presented a study of the Hg(II)/Cu(II)-catalyzed 1-ketone oxidation.

Experimental

Materials

Copper(II) chloride dihydrate (A.R.) was dried at $110^\circ C$ under vacuum and stored in a desiccator before use. Copper(II) chloride (A.R.) was used as purchased. Copper(I) chloride was prepared as described in the literature.¹⁸⁴ Sulphurous(VI) oxide (A.R.), sulphurous(VI) oxychloride (A.R.) and peroxodisulfate sodium octahydrate (A.R.) were used as purchased. The cobalt(II) SCHIZO trim complex, CoSCHIZO, was obtained from P. H. Bevilacqua.¹⁸ Other materials are described in Chapter 3.

Agitation

The CLO spectra were recorded as described in Chapter 2. The pressure levels appearing for oxidation is described in Chapter 2.

Oxidation Potentials

These are described in Chapter 2.

Spectral Studies

These are described in Chapter 2.

Results and Discussion

Oxygen Consumption Dependence

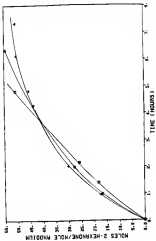
The effect of changing the [Cu/Th] is shown in Figure 30. Increasing the Cu/Th ratio appears to increase the initial rate, however the lifetime also declines more rapidly. For 1 Cu/Th, 51 turnovers are seen in 17.5 hours. For 2 Cu/Th, only 15 turnovers are seen after 12.5 hours. When $\text{Cu}(\text{OH})_2 \cdot 12\text{-H}_2\text{O}$ alone is used as the catalyst for *p*-benzene oxidation with H_2 , no *p*-benzoate is detected.

Wines and coworkers²¹ used a Cu/Th ratio of 2 to most advantage, but they reported that increasing the Cu/Th ratio above 1 did not effect the rate of reaction. (Initial rates were reported to be proportional to the amount of copper when the Cu/Th ratio was less than 1.) Ryberg²² has studied the oxygen consumption at high Cu/Th ratios (1, 4, and 40) and reported that the oxygen specificity decreases

Figure 10:

Selection of 1-jetons (left) and 0, 800, 10, 100 and 500, and 1000 (right) events at $\sqrt{s} = 13.6$ TeV. The numbers in the legend indicate the number of jets in the event. The numbers in the legend indicate the number of jets in the event.

100 100
 100 100
 100 100
 100 100



as the Cu/Se ratio is increased. Sykes also reports that at 70°C, only 1/2 equivalent of copper (based on alcohol) is necessary for oxidase catalytic activity. However, at this temperature, the difference in rates between the BaCl_2 and Ba/Cu -catalyzed reactions is much smaller than at 60°C. The reaction without the copper constituted to 1/2 the rate of the Ba/Cu reaction at 70°C, whereas at 60°C it is only 1/10. This result is consistent with the differences in activation energy for the reactions (Chapter 1). Interestingly, Jones and Isaacs have reported^{11,12} that the Wacker oxidation of alkenes in aqueous solution by rhodium(III) chloride with O_2 as the co-oxidant occurs at 1/10 the rate as when PdCl_2 or CuCl_2 are co-oxidants.

Reaction Pathways in Isopropanol Oxidation

One of the distinguishing features about the Ba/Cu -catalyzed alcohol oxidation is the incorporation of both O atoms of O_2 into 2-ketone products. No solvent reducing equivalents are necessary for this reaction, thus it is almost as active in t-butanol as in ethanol and isopropanol (vide infra). However, these latter alcohols may participate in the reaction by helping form the active catalyst, as suggested by Kinsman and coworkers.

Kinsman and co-workers¹⁰ reported that in the early stages of reaction of the Ba/Cu co-catalyzed alcohol oxidation, acetaldehyde is formed from ethanol solvent oxidation and is rapidly equilibrated anionically with ethoxide. From this

they concluded that Rh(III) was reduced to Rh(I) in an initiation step, forming the active catalyst. Co(III) is also reduced to Co(I) and precipitates as CoS in this step.

Ryberg studied the reaction in isopropyl alcohol,¹² and found that on mixing all the ingredients necessary for the oxidation, only 1/2 equivalent (based on rhodium) of acetone is formed, and this amount remains constant for at least 1/2 hour. Ryberg concluded that only enough acetone was formed as needed for reduction of Co(III) to Co(I) , although this reduction may occur via a rapid reaction with Rh(I) formed initially from elemental oxidation (equation 43). Ryberg correctly points out that simultaneous reduction of both Rh(III) and Co(III) would require 3/2 equivalents of acetaldehyde to be formed (equation 44).

A study of acetone production in Rh/Cu -catalyzed 1-hexene oxidations in isopropyl alcohol was made under conditions similar to those used by Rasmus and co-workers. The results are reported below.

[Rh]	[Cu]	Rh/Cu acetone produced/mole rhodium (hours)			
0.002M	0.002M	0.16(0.08)	0.40(0.15)	1.6 (0.75)	1.2(2.4)
0.002M	0.040M	- (0.08)	0.81(0.15)	3.0 (0.75)	1.9(2.4)
0.002M	-	0.14(0.08)	0.29(0.15)	0.55(0.75)	1.4(2.2)

In these experiments, acetone seems to be produced continuously, but at very low levels compared to the amount of 2-hexanone produced. After 2.5 hours, 2-hexanone production ceased for both the RhCl_3 and Rh/Cu reactions. Acetone

production in the HbCl_2 -catalyzed system is at a rate comparable to that seen for Hb/Cu (8% molar excess), but production continues to increase with time after 2.5 hours in the HbCl_2 system. Uranium is not produced in the Hb/Cu reaction after 2.5 hours. These results differ considerably from those reported by Sykes, but agree for the most part with the observations made by Stone and co-workers.

It appears that uric in the reaction both Hb(III) and Cu(II) may be reduced via alcohol solvent oxidation, which may be the reason that the catalyst is most active in these solvents. However, the uriciny seen in solvents which do not undergo oxidation implies that another route for uriciny initiation exists (vide infra).

The production of H_2O_2 in the Hb/Cu system was also investigated. The results are shown below.

[Cu]	[Hb]	H_2O_2 /uranine (Internal Standard)		
		50 Peak Area Ratio		
0.00400	-	0.187(8)	1.00 (2.1)	0.480(20)
0.00420	0.00400	0.106(8)	0.420(1.8)	1.00 (24)

These reactions were conducted in ethanol solvent, at each lower catalyst concentrations than those employed in the systems production study. These results indicate that even in the Hb/Cu -catalyzed reaction, water is continuously produced, although at much lower levels than in the HbCl_2 -catalyzed system. This indicates that some HbCl_2 -catalyzed reaction is occurring, even in the presence of copper at the lower catalyst concentrations. This implies that uriciny

between the reaction and copper catalysis is necessary for complete activity.

Discussion

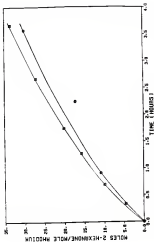
Figure 14 shows a comparison of the Rh/Cu -catalyzed isobutene oxidation in ethanol and *t*-butanol solvents. Unlike the RhCl_3 -catalyzed reaction, which is very slow in *t*-butanol, the Rh/Cu catalysis is quite active in *t*-butanol. This also was reported by Minoue and co-workers,¹⁸ but was not quantified. This reaction inhibition could not occur by solvent reduction of Rh(III) and/or Cu(II) . An alternative "inactivation" of the cycle could involve the Markov-type hydroxylation of olefins by Rh(III) and Cu(II) ; the second half of Minoue's proposed catalytic cycle.

Acetone may also be used as the solvent in this reaction. In this case an induction period of at least nine hours is seen. The addition of hydrogen peroxide after 1.5 hours had no effect on the reaction in acetone. It is possible that a copper catalyzed acid condensation of acetone with itself is occurring in this solvent (as suggested by Syberg), which may partially account for the slowness compared to ethanol and *t*-butanol solvents. A comparison of the reaction in ethanol, *t*-butanol, and acetone solvents is made below.

Figure 10. Reduction of 1-bromo-1-phenylethane (1b) with R_2SiH_2 (0.016 mol), $\text{Pd}(\text{OAc})_2$ (0.003 mmol), R_2SiH_2 (0.003 mmol), temperature = 100°C , pressure = 40 atm.

- a) 1-phenylethanol (4.04), 1-phenylethyl bromide (1.04), 1-phenylethyl acetate (1.04), 1-phenylethyl acetate (1.04), 1-phenylethyl acetate (1.04).
- b) 1-phenylethanol (4.04), 1-phenylethyl bromide (1.04), 1-phenylethyl acetate (1.04), 1-phenylethyl acetate (1.04), 1-phenylethyl acetate (1.04).

(a) 0.75 mmol.
 (b) 1–30 mmol.



<u>Substrate</u>	<u>Yields (%)</u>	
Benzene	27.1(2.7)	
n-Heptane	17.2(1.5)	84.8(34)
Acetone	1.0(1.5)	89.8(33)

As mentioned earlier, acetone is produced when isopropyl alcohol is used as the solvent for this reaction. Alcohol oxidation is the source of aldehyde substrate since no is-ovals only results. The oxidation of 1-hexanol by RuO_4 produces the same amount of 1-hexanoic as the oxidation by KMnO_4 at equivalent reaction concentrations, as reported in Chapter I. This is contrary to Ryberg's assertion²² that OsO_4 is as good at oxidizing alcohols as KMnO_4 , at least for this alcohol.

Effect of Radical Inhibitors

Although it is unlikely that the RuO_4 -catalyzed olefin oxidation proceeds through a free radical chain mechanism, and such a mechanism has been ruled out for the KMnO_4 -catalyzed reaction, it was of interest to observe the effect of radical inhibitors on the reaction. Ryberg pointed out that phenol inhibitors may be oxidized or polymerized by copper catalysts. The inhibitor 8-phenyl-1-octadecylamine was added to a RuO_4 -catalyzed 1-hexene oxidation. As shown in Figure 27, the initial rates are unaffected by the trap. These results indicate that a free radical oxidation is not taking place in this system.

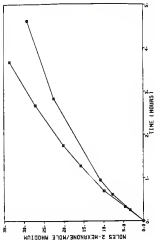
Figure 20.

Oxidation of 1-hexene (100%) with Fe , SnCl_4 (0.130 mmole), and OsO_4 (0.104 mmole) in acetic acid (400 mL). Temperature = 50 °C, pressure = 100 psi H_2 .

Q indicates no substrate added.

R indicates 5-phenyl-1,3-cyclohexadiene (0.81 mmole, 20 mol% substrate) (0.81 mmole) added.

(O) 100% H₂O
 (●) 100% Me₂SO



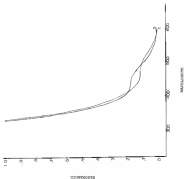
Electron Spin Resonance Spectroscopy

The visible electronic absorption spectrum was taken before and after a HCl/Cu -catalyzed *l*-lysine oxidation. The spectra are shown in Figure 18. Before oxidation, there is one shoulder peak at 498 m μ . After oxidation, this peak has shifted to 495 m μ , indicating loss of chloride ion (vide supra). After reaction is complete, another band appears at long wavelengths (~ 600 m μ). Such peaks are characteristic of copper(II). Thus it appears that significant concentrations of Cu(II) are present after, but not during, the reaction.

The ESR spectrum was also monitored before, during, and after oxidation. Signals were removed from the reaction mixture and the ESR spectrum recorded. As seen in Figure 19, there are two well-resolved signals. Each exhibits a four-line hyperfine. In both cases, $g_{\perp} = 2.04$. The signal with $g_{\parallel} = 2.04$ is similar to the signal seen in the HCl/Cu -catalyzed oxidation (Chapter 10), with $a_{\parallel} = 110$ G. The other signal is somewhat stronger, with $g_{\parallel} = 2.37$ and $a_{\parallel} = 120$ G. This signal is likely due to Cu(II) , which is present in solution even during *l*-lysine oxidation. This is significant because it implies that $\text{Cu(I)}/\text{Cu(II)}$ redox reactions are occurring in the *l*-lysine oxidation. After oxidation, the hyperfine of the spectrum becomes complicated, and $g_{\perp} = 2.08$ and $g_{\parallel} = 2.37$. Thus it seems that the copper-like ESR signal seen in the HCl/Cu -catalyzed oxidation is not due to $\text{Cu(NO}_3)_2$ in solution, although it may well be due to another copper complex.

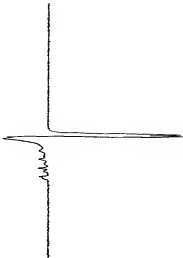
Figure 10.

Visible spectra recorded during the oxidation of 1-benzen (1360.1) with α - α Cl₂, (13, 136, 1360.1) and (1360.1) (13, 136, 1360.1) in alcohol (1360.1). Temperature is 10°C, pressure = 10000.0. Even the reaction mixture of 1-benzen with α - α Cl₂ was dominated. Spectrum 1 was initiated before reaction. Spectrum 2 was recorded after 15 hours.



100

1956-1957 season. The following table shows the results of the survey. The first column shows the number of birds seen, the second column shows the number of birds seen in the morning, the third column shows the number of birds seen in the afternoon, and the fourth column shows the number of birds seen in the evening.



Effect of the Catalyst Precursor

The effect of changing the catalyst precursor for the Et_2Co -catalyzed system was also studied. Shown in Figure 43 is a comparison of 1-hexene oxidation rates with $\text{EtCl}_2 \cdot 2\text{Et}_2\text{O}$ and $\text{Co}(\text{SO}_4)_2 \cdot 18\text{Et}_2\text{O}$ (1 mole Co/mole Rh) and with $\text{Et}(\text{CH}_3)_2 \cdot 2\text{Et}_2\text{O}$, CoCl_2 (1 mole Co/mole Rh) and LiCl as the catalyst precursors. There is little difference in these oxidations. Thus, it seems that for the Et_2Co -catalyzed system, as for the EtCl_2 -catalyzed reaction, the catalyst precursor has little effect on 1-hexene oxidation. Both of these experiments involved a total of 3 moles Cl^- /mole Rh.

Less than 3 total moles Cl^- /mole Rh seems to produce less active catalysts. Minowa and co-workers have reported⁴⁷ that $\text{Et}(\text{COO})_2 \cdot 2\text{Et}_2\text{O}$ and CoCl_2 produces an active catalyst, but the amount of 2-hexenone produced in 4 hours reaction time (20 baromeres) is less than that produced with $\text{EtCl}_2 \cdot 2\text{Et}_2\text{O}$ and $\text{Co}(\text{SO}_4)_2(\text{NH}_4)_2$ (126 baromeres). Less 2-hexenone is produced with $[\text{EtCl}(\text{C}_2\text{H}_5)_2]_2$ and $\text{Co}(\text{ClO}_4)_2(\text{NH}_4)_2$ (26 baromeres) and still less with $\text{Et}(\text{ClO}_4)_2 \cdot 2\text{Et}_2\text{O}$ and $\text{Co}(\text{CO}_3)_2(\text{NH}_4)_2$ (1 baromere).

Effect of Chloride Ion

The effect of chloride ion on the Et_2Co -catalyzed 1-hexene oxidation is illustrated in Figure 44. The addition of 3 moles of EtCl per mole of EtCl_2 (for 3 total equivalents of Cl^- per rhodium) greatly reduces the activity for 1-hexene oxidation. This contrasts the behavior seen for

Figure 49.

Condition of L-hexane (100g) with O_2 in solvent (100g). Temperature is 40°C, pressure is 4000g. O_2 indicates full, (0.150 mmole) and $O_2(0.150)$ mmole indicates...
O indicates $O_2(0.150)$ mmole, both O_2 (0.150 mmole) and full (0.150 mmole) indicates...

ON 100% SURFACE WEIGHT OF
 OF 100% 100% 100% 100% 100%

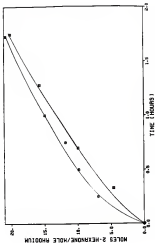
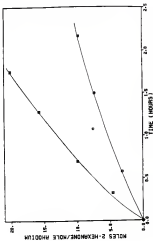


Figure 41.

Collection of 1-phenyl-139c₂ with O₂ in solvent (400h). Temperature = 40°C, pressure = 400h. 139c₂ (0.004 mole), 139c₂ (0.004 mole) and 139c₂ (0.004 mole) were used. 139c₂ (0.004 mole), 139c₂ (0.004 mole), 139c₂ (0.004 mole) and 139c₂ (0.004 mole) were used.



the HbCl_2 -catalyzed reaction, in which the addition of extra Cu^{II} did not affect the reaction. This result agrees with Brown and co-workers' findings⁷⁰ that $\text{HbCl}_2/\text{H}_2\text{O}$ and CuCl_2 produce a much less active catalyst (16 turnovers) than do $\text{HbCl}_2/\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2/\text{CH}_3\text{FA}_3$ (18 turnovers).

Salts of Silver, Zinc, and Copper

As discussed in Chapter 2, Sperry reported⁷² that HbOH and t-buOH are effective oxidants for the HbCl_2 -catalyzed Johnson oxidation, and that HbOH is an oxidant for the Hb/Cu -catalyzed reaction.

Further studies of oxidations using peroxide as oxidant in the Hb/Cu -catalyzed system were also made. The results are shown in Table 5. Several conclusions may be drawn from these results. First with peroxide oxidant, the Hb/Cu -catalyzed system is much faster than the corresponding HbCl_2 reaction. Thus, generation of peroxide by copper alone does not account for the increased catalyst activity, as in the HbCl_2 -catalyzed reaction, t-buOH may be used as the oxidant in this system. In the Hb/Cu -system, oxidized rates with t-buOH are not necessarily faster than with HbOH (as in the case for the HbCl_2 -system), as seen by comparing experiment 28 with 35. In both cases, oxidation is essentially complete within 10 min. As seen in the HbCl_2 -system, the reaction is slower initially in t-buOH . Sperry's data suggest that copper concentration is not critical in the Hb/Cu -system; very little effect on rate or selectivity was

ness when the amount of copper present varied from 0.3 to 1.5 to 1.8 moles copper/mole rhodium. Slightly higher activity was seen when the ratio was 1:1. In our study, the effect of changing the copper concentration seems more pronounced. Comparison of experiment 26 with 27, 28, and 29 indicates that a 1:1 Cu/Rh mole ratio produces the most active catalyst. Even a small excess of copper reduces the activity significantly.

As seen in the HCl_2 -catalyzed oxidations using peroxide, a portion of one Rhodium of peroxide appears to be incorporated into 2-butanone. The results of experiments 24, 26, and 29 seem to indicate that slightly more than one Rhodium may be incorporated (vide infra). Experiments 24, 26, and 29, however, indicate that up to two Rhodium may be used to form 2-butanone. This is unexpected, however, as peroxide requires only two electrons for complete reduction, and two are provided by one molecule of 2-butanone. Incorporation of both Rhodium from HCl_2 into 2-butanone would require some species to require a net of two electrons per Rhodium. Incorporation of both Rhodium from t-BuOOH to even one mole unlikely, as t-butan-2-ol is expected to be provided. For this reason, the possibility of Fischer chemistry occurrence was investigated.

Although Blum and co-workers²⁹ ruled out water as the oxidant in this reaction in the presence of O_2 , the effect of H_2O or an added oxidant in the absence of O_2 was studied for several reasons. First, Blum and co-workers proposed

a Fischer-type oxidation on the second half of their cycle. Also Jones^{12,13} has shown that HfCl_3 and CoCl_2 can be used in a Fischer-type oxidation in the absence of O_2 . (This reaction is stoichiometric in CoCl_2 or FeCl_2 .)

The results of our experiments in the absence of solid oxidant (none trace oxidant is present in the system) are presented in Table 8. As seen in experiments 10 and 16, 1.1 turnovers are produced when the system contains one mole of copper(II) per mole of rhodium(III). Increasing the Cu/Rh ratio from 1.0 to 4.0 increases the 1-butene produced, as shown by experiments 18-28. These results also occur in isopropene and 1-butene systems, as shown by experiments 40-43. The addition of H_2O in experiment 45 does not appear to affect the reaction. As discussed in Chapter I, trace amounts of O_2 in the apparatus could not account for the amount of oxidation seen in these experiments. In the Cu/Co-catalyzed 1-butene oxidation, formation of 0.22 moles of 1-butene (1.1 turnover in these experiments) would require 0.21 moles of O_2 . The solubility of O_2 in undegassed ethanol is $1.07 \times 10^{-3} \text{ M}$. Under reaction conditions, the ethanol solvent would have to contain $1.04 \times 10^{-3} \text{ M}$ O_2 . This exceeds the solubility limit for O_2 in ethanol. The amount of O_2 present when the solution in a 15 ml round bottom flask is 0.22 moles if none is purged out. If a 10 ml flask is used, the amount is 0.093 moles. (Both 10 and 15 ml flasks were used in these experiments.) Thus, it would not be possible to obtain the amount of oxidation

TABLE 4
1-HEXENE PRODUCTION FOR THE Ru/Cu -CATALYZED
OXIDATION OF 1-HEXENE WITH H_2O

Exptl	Solvent	Cat	Water Exptl M	1-Hexene M	Temperature (°C)
25	EtOH	$\text{Ru}/1.0\text{Cu}$	—	1.00	1.80(100) 1.7(100) 1.6(40) 1.7(1.0)
26	EtOH	$\text{Ru}/1.0\text{Cu}$	—	1.00	1.7(100)
27	EtOH	$\text{Ru}/5.0\text{Cu}$	—	1.00	1.7(100) 1.6(100) 1.6(40)
28	EtOH	$\text{Ru}/5.0\text{Cu}$	—	1.00	1.6(100) 1.6(100) 1.7(40)
29	EtOH	$\text{Ru}/6.0\text{Cu}$	—	1.00	4.1(140) 1.0(10)
40	EtOH	$\text{Ru}/1.0\text{Cu}$	—	1.00	1.7(100) 1.6(40) 1.5(1.0)
41	EtOH	$\text{Ru}/6.0\text{Cu}$	—	1.00	1.6(100) 1.6(100) 1.6(1.0)
42	EtOH	$\text{Ru}/1.0\text{Cu}$	—	1.00	.86(100) 1.7(100) 1.3(1.0) .96(25)
43	EtOH	$\text{Ru}/1.0\text{Cu}$	45 H_2O	1.00	1.6(100) 1.6(100) 1.7(1.0) 1.6(1.0)

observed in Table 4 through improper purging technique, it appears that SnCl_4 and $\text{Co}(\text{NO}_2)_2$ are capable of Fischer-type oxidation in this system, as reported by Jones.^{12,13}

$\text{Co}(\text{I})\text{Cl}$ is produced in this reaction with no added oxidant. Acetone production was monitored in the reactions in isopropyl alcohol, and the results are shown below.

Expt.	Acetone Turnover (Hours)		
40	2.60(2.40)	0.36(0.31)	0.34(0.5)
41	0.34(0.25)	1.7 (0.38)	1.5 (1.2)

Trinickles and co-workers have shown^{12f} that $\text{Co}(\text{NO}_2)_2$ is capable of oxidizing diafin with isoduphosphene. To test whether copper(III) might be playing such a role in our system, PdO was used as the oxidant with $\text{Co}(\text{NO}_2)_2$ in both solvent and acetone mixtures at 40°C. Pressure built up in both reactions, blowing out the stops on the flask. No products were observed. In isonitrile solvent (used by Trinickles and co-workers) at room temperature, a ratio of 1:1:1 of 1:1:1 isoduphosphene(III): PdO was used (Trinickles and co-workers used 1:1:1^{12f}). Although PdI was observed, no oxidation products were detected. Similarly, p-OB-OBABO was used as the oxidant in 50/50-methylal:1-hexane mixtures in alcohol solvent at 40°C under H_2 . Only 1.5 turnovers were observed after 3 hours—none were observed with no added oxidant, although the product was not formed immediately. $\text{Co}(\text{NO}_2)_2$ alone in this reaction produced only trace amounts of products.

Labeling Studies

The incorporation of a deuterium label from either solvent ($\text{CD}_3\text{SD}_2\text{O}$) was studied to investigate possible incorporation in the BuNO -catalyzed 1-hexene oxidation with O_2 . Several examples of possible intermediates were given in Chapter 2. It is possible that an alkylperoxocarbonate species such as **2** (Chapter 2) may be formed via a copper catalyzed addition of BuNO to the double bond of 1-hexene activated by coordination to Cu(I) . This species would be analogous to the complex of tBuNO and Ba(Et) described in Chapter 2 and would contain a second molecule of 1-hexene in a similar fashion to tBuNO .

The results shown in Figure 42 indicate that essentially one deuterium atom is incorporated into 2-hexenoic product by comparison of the parent ion peak at m/e 104 with that for unsubstituted 2-hexenoic at m/e 106. A small amount of deuterated product is observed in the peak at m/e 102. Comparison of the approximately equal peaks at m/e 44 and 47 with that for unsubstituted 2-hexenoic at m/e 43 indicates that about 50% of the terminal methyl groups are monodeuterated. Similarly, comparison of the approximately equal peaks at m/e 58 and 63 with that for unsubstituted 2-hexenoic at m/e 61 indicates that about 50% of the carbon adjacent to the carboxyl group is monodeuterated. Figures 43 and 44 show that there is no significant deuterium incorporation into the volatile 1-hexene at the 2-hexenoic internal standard.

Figure 42. Oxidation of 2-benzen (15ml) with O_2 , H_2O_2 (0.148 mmole), and $Os(BR)_2$ (0.125 mmole) in decahydral nitroben (5ml). Temperature = 40°C, pressure = 40psig O_2 . Reaction samples were analyzed with a gas-liquid chromatograph.

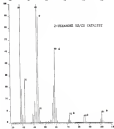
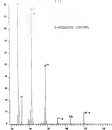
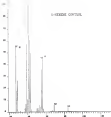


Figure 4B. Oxidation of 2-benzo (13ml) with O_2 , H_2O_2 (0.148 mmole), and $Co(R_2)_2$ (0.131 mmole) to generate ethanal (4ml). Temperature = 40°C, pressure = 48psi O_2 . Reaction samples were analyzed with gas-liquid chromat.

L-LEUCINE CONTROL



L-LEUCINE BLANK CONTROL

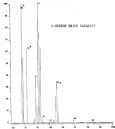
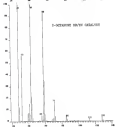
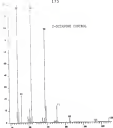


Figure 4d. Oxidation of 1-hexene (2.5ml) with O_2 , UO_2 (0.148 mmole), and $Cr(NO_3)_3$ (0.131 mmole) in decahydrotetrahydrofuran (4.5ml). Temperature = 60°C, pressure = 40psig O_2 . Reaction samples were compared with undisturbed compounds.



This result is significant because it implies that there are two complementary pathways for alkene oxidation, as suggested by Hinson and co-workers.¹⁰⁹ In one pathway, desorption of the terminal methyl group occurs via a β -hydrogen elimination or an equivalent rearrangement. In the other, desorption of the carbon adjacent to the terminal occurs. This could be accomplished through oxidation of 2-butenes. The lack of deuterium incorporation into the 2-butenes (internal) standard implies that oxidation of this isomer does not occur, and suggests that the deuterium incorporation occurs before the product is formed.

Shortly after this experiment was conducted, Boriciol and co-workers reported the results of a similar experiment on this system.¹⁰⁸ Using C_4D_{10} solvent, they found 50% monodeuterated 2-butene product. The disubstituted product was observed. Further, 2-butenes produced by addition of $[C-^2H]$ 2-butenes retained about 50% of the deuterium label. These authors suggested that decomposition of the peroxy- σ -allylcaradiene occurs via a β -hydrogen σ -allylcaradiene or an equivalent rearrangement, followed by decomposition of the σ -allylcaradiene complex in the Wacker step via a metal assisted β -hydride shift. Such a mechanism would explain their observed results. Present, these results are not conclusive. It is possible that other equally plausible mechanisms may give these results. For example, the σ -allylcaradiene hydrometallation may not proceed in the same fashion (β -hydride elimination) as the well studied

pinelidone-antidopamine reaction, Bertolini and co-workers noted that other reactions which were thought to proceed via a peroxymethanesulfonyl intermediate did not demonstrate deviation in similar experiments, implying that these labile esters may in fact decompose via 1-hydrate shift. Thus, the results of this study are inconclusive.

It is very interesting to compare the results reported by Bertolini and co-workers with those reported here. At one point Bertolini mentions methanesulfonyl acid esters to esters, although addition of this acid is not mentioned in the experimental section of the paper. Bertolini's work, like Kinsch's, was conducted at much higher metal concentrations than those employed here. The effect of catalyst concentration on both the SnCl_4 and Sn^{2+} reactions is significant.

Role of Copper

As discussed earlier, these data further distinguished the Sn^{2+} -catalyzed labonone oxidation from that with SnCl_4 . In the presence of copper, both 2 atoms of O_2 are incorporated into ketone product, the reaction rate is greatly increased, and the isomerization of 1-ketone, which occurs in the SnCl_4 system, is not observed. The fact that Sn(II) itself does not appear to oxidize labonone with O_2 , particularly, as indicated above (vide supra) implying that the oxidation mechanism involves two paths for cyclic oxidation, at least one copper-mediated. The fact that no isomerization

of 1-hexene occurs in the presence of copper suggests that with copper, olefin oxidation is accelerated enough to be the favored reaction, or that rhodium(III) hydrides undergo rapid reactions with Cu(I) so that no Cu(I) may be formed, or that the olefin is bound to Cu(I) instead of rhodium.

Because Cu(I) has been reported¹⁰⁹⁻¹²⁰ to be capable of binding olefins, experiments were made to investigate the possibility that Cu(I) could be catalyzing double bond addition to a bound rhodium hydroperoxide species. General approaches were used in this study.

Copper(II) chloride was reacted with 1-hexene and H_2O_2 in nitroac solvent. This reaction was performed under nitrogen. When H_2O_2 was added before 1-hexene, some amount of 1-hexenone and an unidentified product were observed. When 1-hexene was added before H_2O_2 , no 1-hexenone or other products were observed.

Since copper(0) is reported to reduce Cu(II) to Cu(I) in solution, the combinations of $\text{Cu}(\text{NO}_3)_2$ and Cu(0) as copper catalysts were reacted with 1-hexene and t-BuOOH in 1-hexanol at 40°C . No oxidation products were detected in this reaction. Copper metal was also added to an active Rh/Cu -catalyzed 1-hexene oxidation to observe the effect of increasing the concentration of Cu(I) in the solution. The oxidation became very dark in color, most of the copper(0) dissolved. The activity of this combination for 1-hexene oxidation was greatly reduced. After 24 hours, only 8

reactions were observed. This result implies that the Cu(II)/Cu(I) couple is important to 1-hexene oxidation.

Because 1-hexene was shown to couple with Ru(II) (Scheme 3), it was added to a Ru/Cu -catalyzed 1-hexene oxidation to see if a cyclic peroxide could be formed. No high molecular weight products were detected by GC in this reaction.

Although no evidence of a Cu-catalyzed double bond addition was observed, this does not rule out the possibility of this occurring in the mechanism.

Other Studies

Each reaction was added to an active solution to observe the effect. As shown in Figure 43, reaction stops immediately upon CO addition. As for the RuCl_2 -catalyzed reaction, this implies the presence of Ru(II) species. As with RuCl_2 , the visible electronic absorption spectrum taken after CO addition is similar to that for $[\text{Ru(CO)}_2\text{Cl}]_2$.

Characterization of Solid Catalyst

Solid catalyst was recovered from a reaction with a high concentration of RuCl_2 (0.01 M) and Cu(Ru)_2 (0.01 M) by removing the solvent and extracted hexene with a rotary evaporator after oxidation was complete (90 hours). The deep red-brown solid obtained was dried under vacuum at 100°C . The infrared spectrum, recorded as a KBr pellet, is shown in Figure 44. The IR spectrum is identical to that

Figure 45.

Oxidation of 3-Amino-1,2,4,5-tetrahydro-6H-1,2,4-triazine-6-one, and OsO_4 , (bottom series) in acetonitrile (CH₃CN), Temperature = 50 °C, pressure = 100 psi O_2 .
O indicates an O atom.
O indicates an O added after 4.8 hours.

10
 20
 30
 40
 50
 60
 70
 80
 90
 100

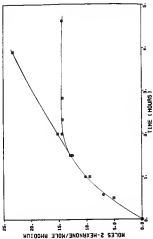
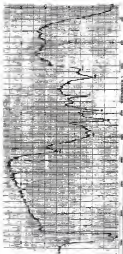


Figure 2b. IR spectrum of the γ -ray $\text{BaCl}_2(\text{Ca}(\text{NO}_3)_2)$ mixed phase between 2000 and 600 cm^{-1} , recorded at 4 K (not in situ).



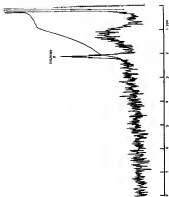
ness for the spent catalyst recovered from a HfCl_3 -catalyzed reaction, described in Chapter 2. Besides the strong band due to Hf-Cl stretch at 333 cm^{-1} (also seen for $\text{HfCl}_3 \cdot 3\text{H}_2\text{O}$), new absorptions appear at 1210, 1715, 1240, 1160, 1000, 1025, and 460 cm^{-1} . ν_{as} , ν_{sym} , bridging hydrazo, hydrido-, alkene, and alkane ligands are possible.

The ^1H NMR spectrum of the spent Hf/Ca catalyst in d -chloroform was also recorded and is shown in Figure 47. Like the HfCl_3 deactivated catalyst, a broad peak is seen between 0.5 and 2 ppm, however, the peak at 3.8 ppm seen for HfCl_3 is absent for Hf/Ca . A peak at 0.1 ppm may be solvent impurity present.

Other Metal Metal Systems

Several other mixed metal catalyzed reactions were attempted to see if the in situ generation of peroxides could apply to other catalysts. Hf/W co-catalyzed 1-hexene oxidations were conducted in ethereal solvent at 40°C and 40 psi O_2 using both HfCl_3 (4.5 equivalents based on Hf) and HfCl_3Cl_3 (one equivalent based on Hf). In both cases, 2-hexenoic acid produced along with another product which appeared to be 3-hexenoic acid or epoxide. Ti/Zr , Ce/W , Hf/Ca/W , and Ce/W (called as CeOEP^{TM}) catalyzed 1-hexene oxidations were conducted. The Ce/W reaction, conducted at 70°C , produced only trans products. The Hf/Ca/W system produced only 2-hexenoic as a major product. The Ce/W reaction, conducted at 80°C , produced 2-hexenoic and

Figure 4.7. $\frac{1}{2}\pi$ phase rotation of the output $\text{Re}(U_1)/\text{Re}(U_2)$ cascade
in $d_{\text{quadrature}}$.



1-hexanol, as expected for the Co/SPT catalyst in the absence of Ru. The choice of alcohol solvent in these reactions was a poor one, since alcohol inhibits Ru-catalyzed reactions severely. It would be interesting to attempt the Ru/Cu/Ru-catalyzed 1-hexene oxidation in a non-alcohol solvent, since the Ru/Cu-catalyzed reaction does not require alcohol to release Ru(III).

Other reactions attempted were Cu/Cu (Cu as Co/SPT) and Ru/Cu (Ru as RuCl_3 and $\text{Ru}(\text{PPh}_3)_3/\text{O}_2$) co-catalyzed 1-hexene oxidations in ethanol solvent. The Cu/Cu reaction, conducted at 40°C produced 1-hexanol, 1-hexanal, and another product. The Ru/Cu reaction, conducted at 40°C and 10°C , produced only 1-hexanol, although not as much as the corresponding Ru/Cu system. A Ru/Pd catalyst (Pd as $[\text{Pd}(\text{OAc})_2]_2$) produced mainly 2- and 3-hexanone. A black deposit at Pd(0) was produced in this reaction. A Pd/Cu catalyst (Pd as $[\text{Pd}(\text{OAc})_2]_2$) produced only small amounts of 1-hexanone, along with Pd(II). There was no Cl⁻ in any reaction.

Reaction Mechanism

A mechanism proposed for this system must account for the pronounced increase in rate and the incorporation of both 0-atoms of O_2 into the ketone product that results by adding copper(II) to the rhodium(III) catalyst. In the Ru/Cu system, copper(II) may play several roles.

The role of Cu(II) in the catalytic mechanism of RhCl_3 in the isomerization step, shown in equation 4b, forming the rhodium(III)-cobaltate complex. This step is a normal step process involving the added reduction of RhCl_3 to a rhodium(I) complex, followed by reaction with the Cu(II) ions to form RhCl_2^+ , CuCl and CuCl_2 . This cobaltate inhibition process was suggested earlier.^{69,72}

A second role for copper ion concerns its involvement in the reduction of O_2 to H_2O_2 . It was reported earlier that cobalt reacts slowly with O_2 to form acetaldehyde and H_2O ,⁷³ both copper(II) and rhodium(III) may catalyze this reaction, presumably via the intermediacy of Cu(I) or Rh(I) species or both. The $\text{Cu(II)}/\text{Rh(III)}$ couple is proposed to play a key role in the Schenck oxidation by reducing O_2 to peroxide. This may occur via the anti-electron reduction to superoxide, which is then converted to H_2O_2 .¹¹¹ The H_2O_2 is quickly captured by the rhodium(III) catalyst, forming RhOOR . This in effect corresponds to a copper-catalyzed path for forming the same RhOOR species involved in the RhCl_3 -catalyzed reaction. Further substantiation for H_2O_2 intermediacy in the O_2 oxidation is provided by the high selectivities and reaction rates reported in Table 3 for the $\text{Rh(III)}/\text{Cu(II)}$ -catalyzed H_2O_2 oxidations of 1-butene to nitroal. This proposal differs substantively from the original suggestion that the catalytic cycle begins with the formation of a coordination complex between rhodium(I) and O_2 .

Consistent with the view proposed by Nyberg's¹² observation that the specificity of these 1-hexene oxidations decreases as the Cu/Rh ratio is increased from 2:1 to 4:1 and 8:1. At higher copper concentrations, the decomposition of RhOH to Rh_2O and O_2 becomes more favorable, as was noted for the direct RhOH cyclic oxidations. Therefore, the decreased specificity of the Rh(III)/Cu(II) catalyst at high Cu/Rh ratios is a result of the increasing importance of the overall four-electron reduction of O_2 to H_2O in copper-catalyzed reactions 18 relative to the cyclic oxidation by intermediary of RhOH in reaction 15.

The mechanism we proposed to account for the Rh(III)/Cu(II) results (Figures 46 and 49). Both incorporate the earlier discussed inhibition and Rh(II)/Rh(III) O_2 reduction steps, forming RhOH. These suggested mechanisms also accommodate the reported reaction kinetics for the Rh(III)/Cu(II) O_2 oxidations, which are here noted as [R₂]. The next two steps in the catalytic cycle in Figure 46 involve the reaction of RhOH with alkene as discussed previously for the rhodium only case. A similar (unproven) five-membered metallacycle intermediate has been proposed by Noyori and coworkers,⁴⁵ and we suggested copper could play a role similar to that involved in Noyori chemistry to allow reaction of of Rh(III)OH with alkene to form ketone and rhodium(I). The subsequent fast oxidation of rhodium(I) to the Rh(III) catalyst by two copper(II) ions is the final step reforming CuCl, completing the cycle. The mechanism

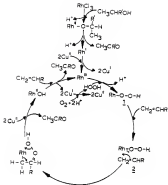


Figure 88. The mechanism for the $\text{RhCl}_3/\text{Cu}(\text{PPh}_3)_3$ -catalyzed oxidation of 1-butene with O_2 .

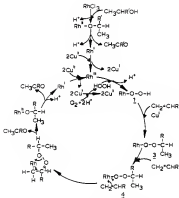


Figure 10. The mechanism for the $\text{RhCl}_3/\text{CuClO}_4$ catalyzed oxidation of 5-hexene with S_2O_8 .

showing copper facilitates copper ion transfer from $\text{Hg}(\text{II})\text{OH}$ to stibic to not well understood, just as we do not understand these details in Wacker chemistry. The fact that $\text{Hg}(\text{II})/\text{Cu}(\text{II})$ will oxidize stibic in the absence of any added oxidant (none added is present in the system) suggests that a Wacker type hydroxymercuration is occurring in this system. This reaction appears to be stoichiometric in $\text{Cu}(\text{II})$ in the absence of O_2 , as expected.

In the second proposal (Figure 4f) copper(II) catalyzes the addition of HNO_3 to the stibinic double bond of an alkene, producing a stibinic allylphenanthroline species, 2, attempts to demonstrate this type of chemistry were unsuccessful. However, $\text{Cu}(\text{II})$ is well known to bind alkenes,^{109,110} including 2-butenes,¹²¹ making them more electrophilic. In cases of stibic or stibinate these adducts.¹²¹ The oxidation of alkenes (including simple alkenes) with $\text{Cu}(\text{NO}_3)_2$ has been reported.¹⁰⁷ HNO_3 species similar to 2 have been characterized for $\text{M} = \text{Co}$,¹¹² Cu ,^{144,113} Fe ,^{11,10,14} and Pt .^{14,14} Ions are capable of stabilizing ferrocenyl alkenes as allylic ketones.^{14,14,15,16,115} Intermediates 2 may attack a second mole of alkene to form the four-center-type intermediates 2. In this case, the product is known and a $\text{Hg}(\text{II})$ alkyl species which decomposes as in the catalytic mechanism step to form $\text{Hg}(\text{I})$ and nitrate. Electron transfer from $\text{Hg}(\text{I})$ to copper(II) completes the cycle, reforming HgCl_2^+ and $\text{Cu}(\text{I})$.

Catalyst Deactivation

Based on the similarities of the visible electronic absorption spectra, IR and NMR spectra for the deactivated catalyst from the SnCl_2 and Sn(III)/Cu(II) systems, it is assumed that the mechanism of deactivation is also similar. Less water is formed in the Sn/Cu -catalyzed reaction, however, a considerable amount of water is present and it is likely that water contributes to catalyst deactivation.

The Sn/Cu catalyst, like the SnCl_2 catalyst, deactivates more rapidly at high concentrations. Thus, a multi-order decomposition mechanism in which one or hydroxy-bridged chains or oligomers are formed is likely. The Sn/Cu catalyst is much more sensitive to the chloride ion concentration than is SnCl_2 , so the loss of Cl^- from the catalyst as the reaction progresses is likely related to deactivation time.

CHAPTER 4 SUMMARY AND CONCLUSIONS

The homogeneous oxidation of 1-hexene by $\text{Rh}(\text{Cl})_3/\text{Cu}(\text{Cl})_2$ was studied because this reaction was reported²⁸ to be the first good example of a selective, controlled oxidation of an olefin with O_2 . In this reaction, terminal olefins are oxidized to 2-hexenols with incorporation of both copper atoms of O_2 into ketone product. The related reaction with RhCl_3 was also studied because of its similarities to the Rh/Cu system and because it was presumed to be a simpler reaction.

The mechanism originally proposed by Basso and co-workers²⁹ for this reaction involved two steps. A $\text{Rh}(\text{I})$ -olefin complex reacts with O_2 in the first step to produce ketone and $\text{Rh}^{\text{III}}\text{OH}$. The rhodium(II) catalyst is regenerated via the oxidation of olefin by $\text{Rh}^{\text{III}}\text{OH}$ in a Vacker-type process in the second step. Since oxidation also occurs in the absence of copper, copper was not thought to play a direct role.

However, a subsequent study of this reaction by Eyring and co-workers^{32,33} reported that in the absence of copper, only one copper atom was used to form ketone.

alcohol solvent was proposed to retain the second oxygen atom. Further, it was suggested that the active catalyst was a $\text{Th}(\text{III})$ complex, not $\text{Th}(\text{II})$, and that peroxides were effective solvents in this reaction.

Both the ThCl_3 and the Th/Ce systems were found to be more complex than originally thought. Experimental evidence in Chapter I has shown that in the ThCl_3 system aldehyde or ketone (from alcohol oxidation) and H_2O are formed continuously with 2-butanone in primary or secondary alcohol solvent and competing side-chain oxidation and olefin isomerization reactions occur, although it was reported⁷³ that in the oxidation with ThCl_3 only one oxygen atom is incorporated into 2-butanone product. Evidence in Chapter I has shown that ThCl_3 is capable of transferring both oxygen atoms to 2-butanone (though this need not be occurring in primary or secondary alcohol solvent). It was also shown in Chapters I and II that the oxidations with H_2O_2 and tBuOOH are very similar to the oxidations with O_2 . In Chapter I it was shown that the presence of copper(II) facilitates a Fenton-type oxygen transfer in the absence of O_2 or peroxide and that an alternate initiation step for the Th/Ce system must exist in solvents such as *n*-butanol and acetone.

Mechanisms have been proposed for each of these catalytic systems which account for the experimental observations (Chapters I and XI). It appears that the Th/Ce mechanism does proceed via a two step mechanism in which the first step is the formation and decomposition of a peroxothallacycle

and the second step is a Wacker-type hydroxyacetalization, unlike the mechanism proposed by Kinsman and co-workers,⁵⁹ the peroxyhydrodiacyls is formed from the reaction of BaOOR with olefin. The ROOR is formed from the reaction of Ba(III) with ROOR. The ROOR is formed by reduction of O_2 with Cu(I) . An alternative mechanism is which Cu(I) accelerates the addition of ROOR to the olefinic double bond to produce ROOR (which may react with a second olefin molecule), similar to the *l*-lysine oxidation with BaOOR , cannot be ruled out.

In the absence of copper, only one copper atom of O_2 appears to be incorporated into ketone product. Here, ROOR is produced via a cycle in which olefin solvent is continuously oxidized. (In low copper concentrations, some olefin oxidation may also occur via this route.) This proposal is also markedly different from Kinsman's proposed mechanism. However, in ketonized solvent, which cannot be reduced, slow catalytic oxidation is observed. A mechanism for such an oxidation may be envisioned in which a Wacker-type hydroxyacetalization of olefin by Ba(III) occurs, producing ketone and Ba(I) , which may bind O_2 , similar to Kinsman's proposed cycle, but with a different starting point.

Thus, copper does appear to be necessary for utilization of both copper atoms to form ketone product. Under some circumstances, rhodium appears to be capable of, but much less efficient at, such utilization.

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